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SPIRO COMPOUNDS AND THEIR USE AS ELECTROLUMINESCENT MATERIALS  
[Spiroverbindungen und ihre Verwendung als  
Elektrolumineszenzmaterialien]

D. Lupo, et al.

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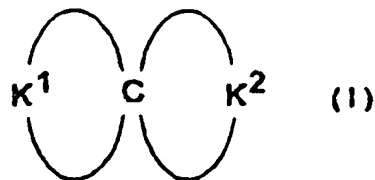
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INVENTOR	(72):	Lupo, D.; Salbeck, J.; Schenk, H.; Stehlin, T.; Stern, R.; Wolf, A; Kreuder, W.
APPLICANT	(71):	Hoechst Aktiengesellschaft
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The use of spiro compounds of the general formula (I)

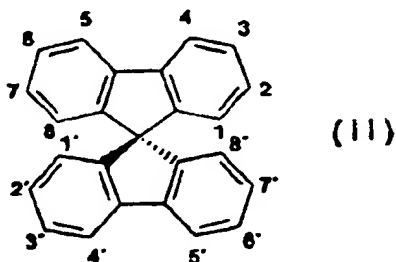


where

$K^1$  and  $K^2$ , independently of each other, are conjugated systems in electroluminescence devices.

Preferred compounds of the formula (I) are 9,9'-spirobifluorene derivatives of the formula (II).

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where the benzo groups, independently of each other, can be substituted.

compounds of the formula (I) are characterized by good solubility in common organic solvents, improved film-forming properties, and a markedly reduced tendency to crystallize out. This makes the production of electroluminescence devices easier and extends their lifetime.

There is a great need in industry for large-surface-area solid- /3 state light sources for a number of applications, primarily in the area of display elements, video display technology, and lighting engineering. At present, the demands placed on these light sources cannot be fully met by any of the existing technologies.

As an alternative to conventional display elements, such as incandescent lamps, gas-discharge lamps, and nonluminescent liquid

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\* Numbers in the margin indicate pagination in the foreign text.

crystal display elements, electroluminescence (EL) materials and devices, such as light-emitting diodes (LED), have been known for some time now.

Electroluminescent materials are substances that are capable of radiating light when an electric field is applied. The physical model used to describe these effects is based on the radiating recombination of electrons and electron gaps ("holes"). In light-emitting diodes, the charge carriers are injected into the electroluminescent material through the cathode or anode. Electroluminescence devices contain a luminescent material as the light-emitting layer. Electroluminescent materials and devices are described in general terms, for example, in Ullmann's Encyclopedia of Industrial Chemistry, Vol. A9, 5th Ed. VCH Verlag, 1987 and in the literature cited there. In addition to inorganic materials, such as ZnS/Mn or GaAs, organic compounds are also known as EL materials.

A description of EL devices that contain low-molecular organic EL materials may be found, for example, in US 4,539,507.

The disadvantages of these low-molecular organic materials are, for example, their insufficient film-forming properties and a marked tendency toward crystallization.

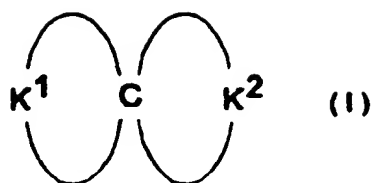
In recent times, polymers have also been described as EL materials (see, for example, WO-A 90/13148). However, the light yield (quantum efficiency) of such materials is much lower than that of the low-molecular compounds.

It would be desirable to find EL materials with good light yields and that, at the same time, can be worked into thin, homogeneous films that have a low tendency to crystallize.

Surprisingly, it has now been found that spiro compounds, in particular derivatives of 9,9'-spirobifluorene, are quite well suited as EL materials.

Individual compounds of this kind are described, for example, in US-A 5,026,894, J. M. Tour, et al., J. Am. Chem. Soc. 112 (1990) 5662 and J. M. Tour et al. Polym. Prepr. (1990) 408 as linking elements for polymeric organic semiconductors and proposed as materials for molecular electronics. Nothing is said, however, of their possible use as EL materials.

Thus, the subject matter of the present invention is the use of spiro compounds of the general formula (I),

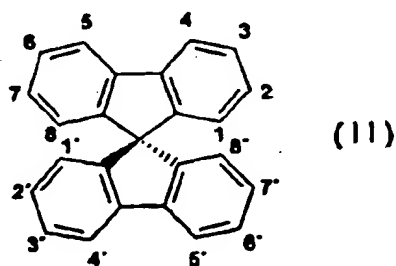


where

$K^1$  and  $K^2$ , independently of each other, are conjugated systems in electroluminescence devices.

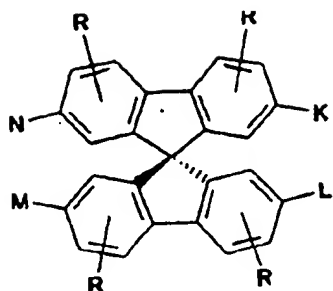
compounds of the formula (I) are characterized by good solubility in common organic solvents, improved film-forming properties, and a markedly reduced tendency to crystallize out. This makes the production of electroluminescence devices easier and extends their lifetime. The emission properties of the compounds used in accordance with this invention can be adjusted over the entire range of the visible spectrum by the choice of suitable substituents. Moreover, the covalent bonding arrangement of the two parts of the spiro compound permits a molecular structure, such that the two halves of the molecule can possess independently adjusted properties. Thus, one half may possess charge-transport or charge-injection properties, for example, while the other has light-emitting properties. The spatial proximity of the two halves, fixed by the covalent linkage, is favorable for energy transfer (see, for example, B. Liphardt, W. Lüttke, Liebig's Ann. Chem. (1981) 1118).

Preferred compounds of the formula (I) are 9,9'-spirobifluorene derivatives of the formula (II),



where the benzo groups, independently of each other, can be substituted and/or fused.

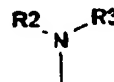
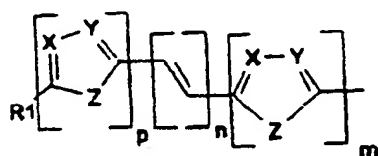
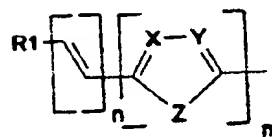
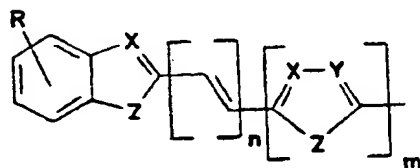
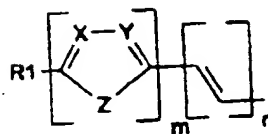
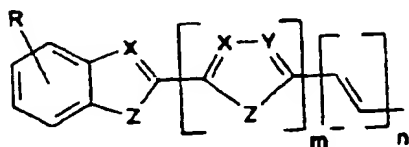
More preferable are spirobifluorene derivatives of the formula (III),



(III)

where the symbols and superscripts have the following meanings:

K, L, M, N are identical or different



R is identical or different and can have the same meanings as K, L, M, N or is -H, a linear or branched alkyl, alkoxy, or ester group with 1 to 22, preferably 1 to 15, more preferably 1 to 12 C atoms, -CN, -NO<sub>2</sub>, -NR<sup>2</sup>R<sup>3</sup>, -Ar, or -O-Ar;

Ar is phenyl, biphenyl, 1-naphthyl, 2-naphthyl, 2-thienyl, 2-furanyl, where each of these groups may have one or two R residues,

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m, n, p are 0, 1, 2, or 3;

X, Y are identical or different and are CR or nitrogen;

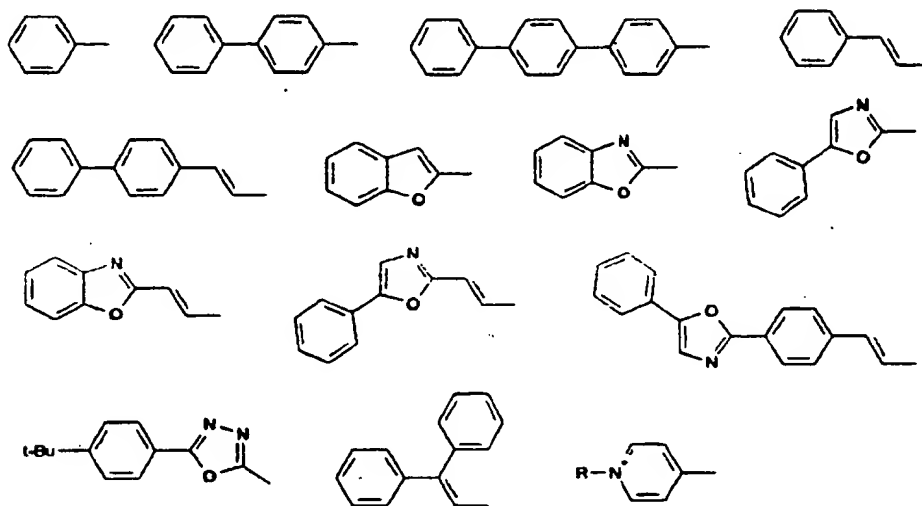
Z is -O-, -S-, -NR<sup>1</sup>-, -CR<sup>1</sup>R<sup>4</sup>-, -CH=CH-, -CH=N-;

R<sup>1</sup>, R<sup>4</sup> are identical or different and can have the same meaning as R;

R<sup>2</sup>, R<sup>3</sup> are identical or different and are H, a linear or branched alkyl group with 1 to 22 C atoms, -Ar, 3-methylphenyl.

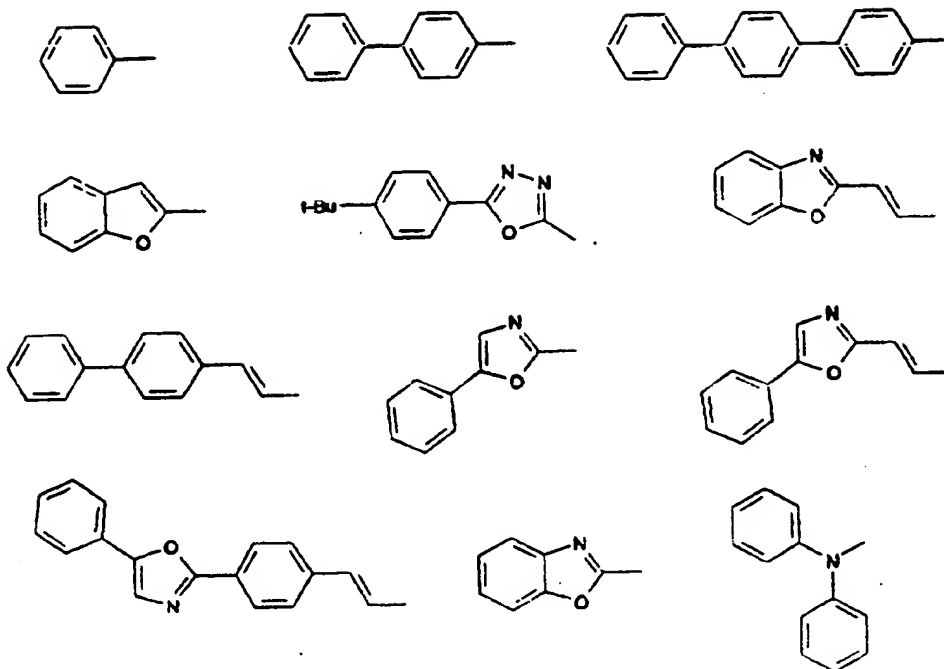
Preferred compounds of the formula (III) are those of the formula (IIIa) - (IIIg)

IIIa) K = L = M = N and are from the group:

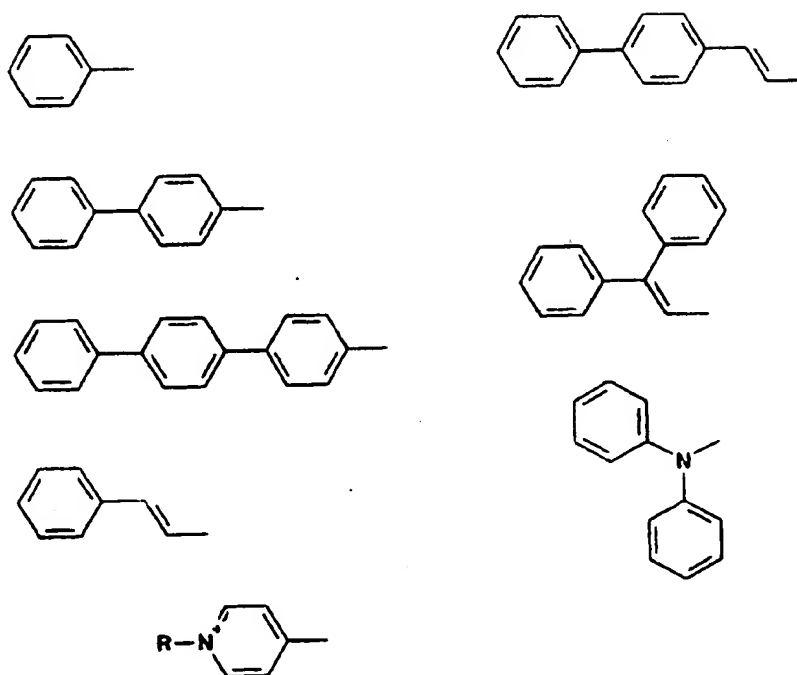


R = alkyl, C<sub>2</sub>H<sub>4</sub>SO<sub>3</sub>-R = C<sub>1</sub>-C<sub>22</sub>-alkyl, C<sub>2</sub>H<sub>4</sub>SO<sub>3</sub>-

IIIb) K = M = H and N = L and are from the group:

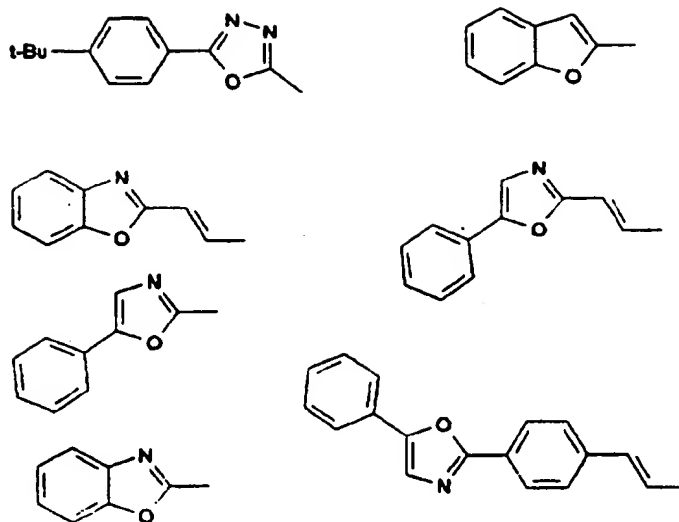


IIIc) K = M and are from the group:

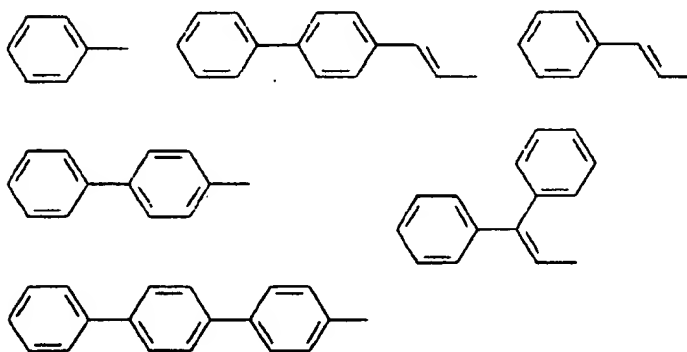


R = alkyl,  $\text{C}_2\text{H}_4\text{SO}_3^-$ , and N = L and they are from the group:

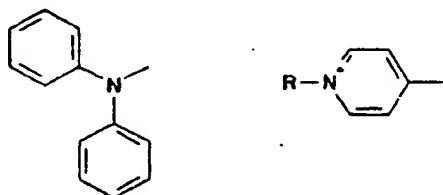




IIIId) K = M and they are from the group:

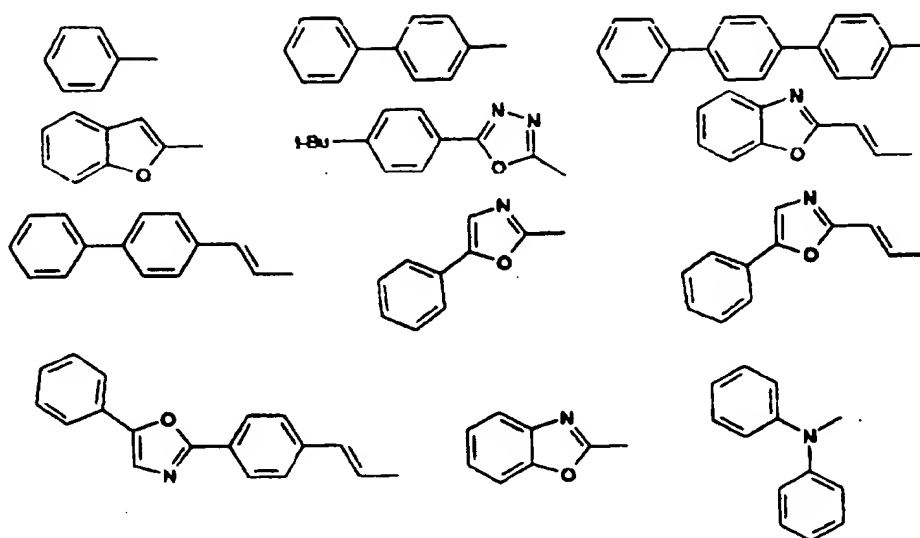


and N = L and they are from the group:

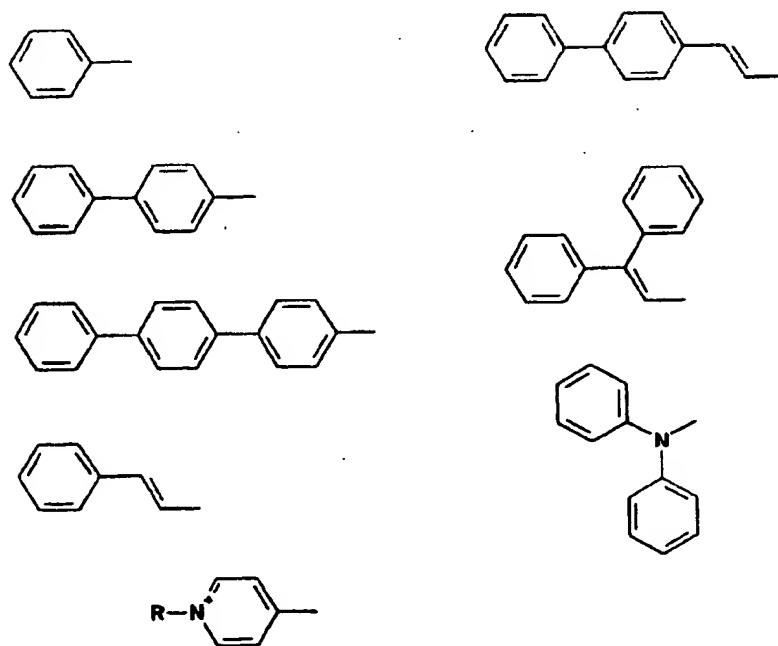


R = alkyl,  $C_2H_4SO_3^-$   
IIIe)

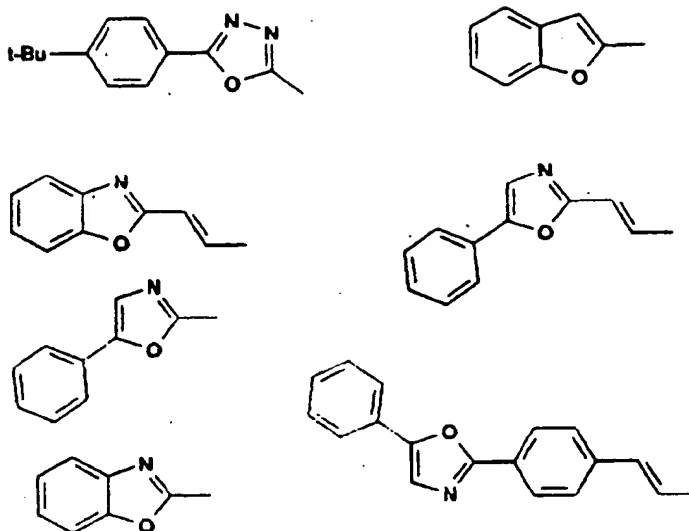
K = L = H and M = N and they are from the group:



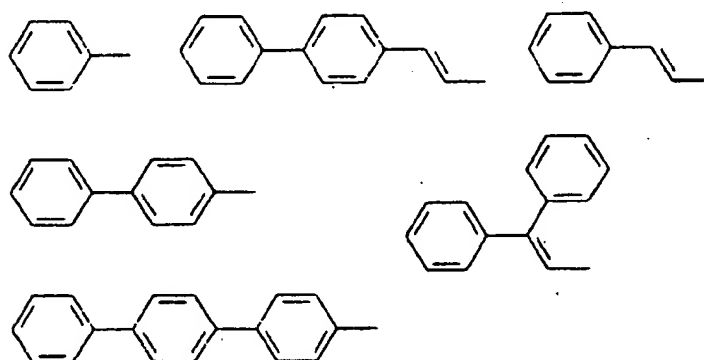
IIIIf) K = L and they are from the group:



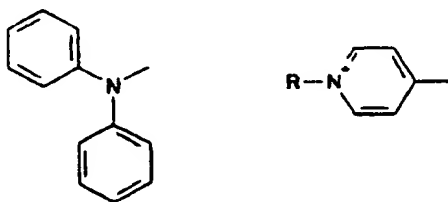
R = alkyl,  $\text{C}_2\text{H}_4\text{SO}_3^-$  and M = N and they are from the group:



IIIg) K = L and they are from the group:



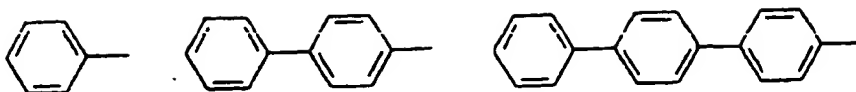
and M = N and they are from the group:



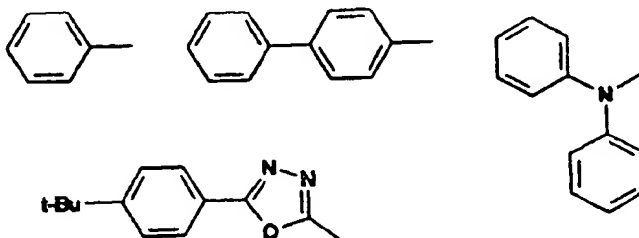
R = alkyl,  $\text{C}_2\text{H}_4\text{SO}_3^-$

More preferred compounds of the formula (III) are those of the formulas (IIIa) to (IIIdb):

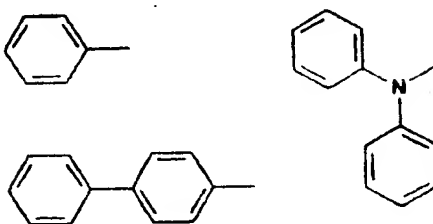
(IIIa) K = L = M = N and they are from the group:



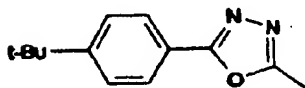
IIIba)  $K = M = H$  and  $N = L$  and they are from the group:



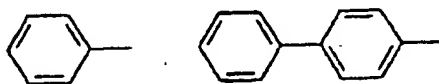
(IIIca)  $K = M$  and they are from the group:



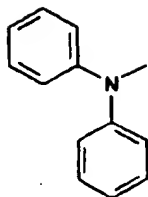
and  $N = L$  and they are:



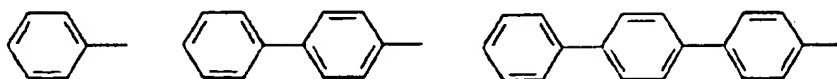
(IIIIda)  $K = M$  and they are from the group:



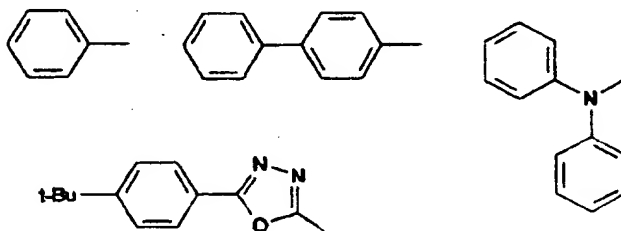
and  $N = L$  and they are:



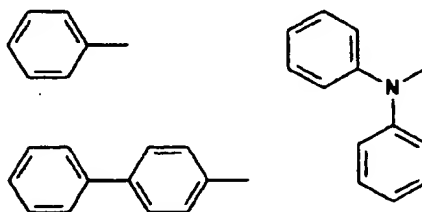
(IIIiab)  $K = L = M = N$  and they are from the group:



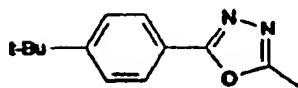
(IIIibb)  $K = L = H$  and  $M = N$  and they are from the group:



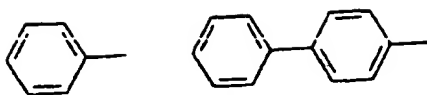
(IIIicb)  $K = L$  and they are from the group:



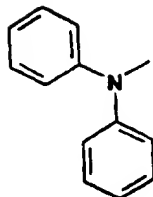
and  $M = N$  and they are:



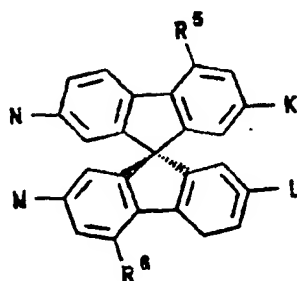
(IIIIdb)  $K = L$  and they are from the group:



and  $M = N$  and they are:



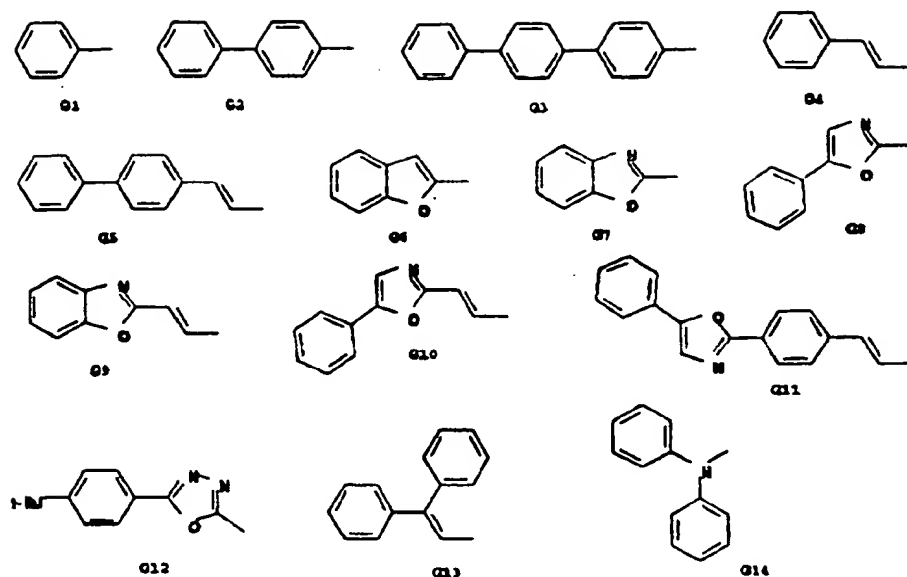
The most preferred spiro compounds are those of the formula (IV),



(IV)

where the symbols have the following meanings:

K, L, M, N, R<sup>5</sup>, R<sup>6</sup> are identical or different and are one of the groups G1 to G14:



and

$R^5$ ,  $R^6$  can also be identical or different and be hydrogen or a linear or branched alkyl, alkyloxy, or ester group with 1 to 22 C atoms, -CN or -NO<sub>2</sub>.

More preferable spiro compounds of the formula (IV) are 2,2',4,4',7,7'-hexakis(biphenyl)-9,9'-spirobifluorene, 2,2',4,4',7,7'-hexakis(terphenyl)-9,9'-spirobifluorene, and the compounds listed in table 1, where the abbreviations G1 to G14 have the meanings indicated in formula (IV).

Table 1: spiro compounds of the formula (IV)  
 $R^5 = R^6 = \text{hydrogen}$

Verbindung	K	L	M	N
Spiro-1	G1	G1	G3	G3
Spiro-2	G1	G1	G4	G4
Spiro-3	G1	G1	G5	G5
Spiro-4	G1	G1	G6	G6
Spiro-5	G1	G1	G7	G7
Spiro-6	G1	G1	G8	G8
Spiro-7	G1	G1	G9	G9
Spiro-8	G1	G1	G10	G10
Spiro-9	G1	G1	G11	G11
Spiro-10	G1	G1	G12	G12
Spiro-11	G1	G1	G13	G13
Spiro-12	G1	G1	G14	G14
Spiro-13	G2	G2	G2	G2
Spiro-14	G2	G2	G3	G3
Spiro-15	G2	G2	G4	G4

Key: Verbindung=Compound



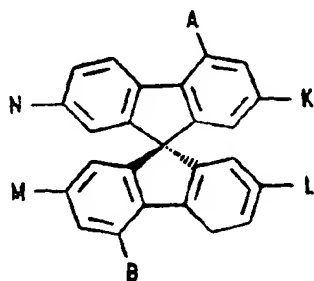
Spiro-16	G2	G2	G5	G5
Spiro-17	G2	G2	G6	G6
Spiro-18	G2	G2	G7	G7
Spiro-19	G2	G2	G8	G8
Spiro-20	G2	G2	G9	G9
Spiro-21	G2	G2	G10	G10
Spiro-22	G2	G2	G11	G11
Spiro-23	G2	G2	G12	G12
Spiro-24	G2	G2	G13	G13
Spiro-25	G2	G2	G14	G14
Spiro-26	G3	G3	G3	G3
Spiro-27	G3	G3	G4	G4
Spiro-28	G3	G3	G5	G5
Spiro-29	G3	G3	G6	G6
Spiro-30	G3	G3	G7	G7
Spiro-31	G3	G3	G8	G8
Spiro-32	G3	G3	G9	G9
Spiro-33	G3	G3	G10	G10
Spiro-34	G3	G3	G11	G11
Spiro-35	G3	G3	G12	G12
Spiro-36	G3	G3	G13	G13
Spiro-37	G3	G3	G14	G14
Spiro-38	G4	G4	G4	G4
Spiro-39	G5	G5	G5	G5
Spiro-40	G6	G6	G6	G6
Spiro-41	G7	G7	G7	G7
Spiro-42	G8	G8	G8	G8
Spiro-43	G9	G9	G9	G9

Spiro-44	G10	G10	G10	G10
Spiro-45	G11	G11	G11	G11
Spiro-46	G12	G12	G12	G12
Spiro-47	G13	G13	G13	G13
Spiro-48	G14	G14	G14	G14
Spiro-49	H	H	G3	G3
Spiro-50	H	H	G4	G4
Spiro-51	H	H	G5	G5
Spiro-52	H	H	G6	G6
Spiro-53	H	H	G7	G7
Spiro-54	H	H	G8	G8
Spiro-55	H	H	G9	G9
Spiro-56	H	H	G10	G10
Spiro-57	H	H	G11	G11
Spiro-58	H	H	G12	G12
Spiro-59	H	H	G13	G13
Spiro-60	H	H	G14	G14
Spiro-61	G1	G3	G3	G1
Spiro-62	G1	G4	G4	G1
Spiro-63	G1	G5	G5	G1
Spiro-64	G1	G6	G6	G1
Spiro-65	G1	G7	G7	G1
Spiro-66	G1	G8	G8	G1
Spiro-67	G1	G9	G9	G1
Spiro-68	G1	G10	G10	G1
Spiro-69	G1	G11	G11	G1
Spiro-70	G1	G12	G12	G1
Spiro-71	G1	G13	G13	G1

<b>Spiro-72</b>	<b>G1</b>	<b>G14</b>	<b>G14</b>	<b>G1</b>
<b>Spiro-73</b>	<b>G2</b>	<b>G4</b>	<b>G4</b>	<b>G2</b>
<b>Spiro-74</b>	<b>G2</b>	<b>G5</b>	<b>G5</b>	<b>G2</b>
<b>Spiro-75</b>	<b>G2</b>	<b>G6</b>	<b>G6</b>	<b>G2</b>
<b>Spiro-76</b>	<b>G2</b>	<b>G7</b>	<b>G7</b>	<b>G2</b>
<b>Spiro-77</b>	<b>G2</b>	<b>G8</b>	<b>G8</b>	<b>G2</b>
<b>Spiro-78</b>	<b>G2</b>	<b>G9</b>	<b>G9</b>	<b>G2</b>
<b>Spiro-79</b>	<b>G2</b>	<b>G10</b>	<b>G10</b>	<b>G2</b>
<b>Spiro-80</b>	<b>G2</b>	<b>G11</b>	<b>G11</b>	<b>G2</b>
<b>Spiro-81</b>	<b>G2</b>	<b>G12</b>	<b>G12</b>	<b>G2</b>
<b>Spiro-82</b>	<b>G2</b>	<b>G13</b>	<b>G13</b>	<b>G2</b>
<b>Spiro-83</b>	<b>G2</b>	<b>G14</b>	<b>G14</b>	<b>G2</b>
<b>Spiro-84</b>	<b>G3</b>	<b>G4</b>	<b>G4</b>	<b>G3</b>
<b>Spiro-85</b>	<b>G3</b>	<b>G5</b>	<b>G5</b>	<b>G3</b>
<b>Spiro-86</b>	<b>G3</b>	<b>G6</b>	<b>G6</b>	<b>G3</b>
<b>Spiro-87</b>	<b>G3</b>	<b>G7</b>	<b>G7</b>	<b>G3</b>
<b>Spiro-88</b>	<b>G3</b>	<b>G8</b>	<b>G8</b>	<b>G3</b>
<b>Spiro-89</b>	<b>G3</b>	<b>G9</b>	<b>G9</b>	<b>G3</b>
<b>Spiro-90</b>	<b>G3</b>	<b>G10</b>	<b>G10</b>	<b>G3</b>
<b>Spiro-91</b>	<b>G3</b>	<b>G11</b>	<b>G11</b>	<b>G3</b>
<b>Spiro-92</b>	<b>G3</b>	<b>G12</b>	<b>G12</b>	<b>G3</b>
<b>Spiro-93</b>	<b>G3</b>	<b>G13</b>	<b>G13</b>	<b>G3</b>
<b>Spiro-94</b>	<b>G3</b>	<b>G14</b>	<b>G14</b>	<b>G3</b>
<b>Spiro-95</b>	<b>H</b>	<b>G3</b>	<b>G3</b>	<b>H</b>
<b>Spiro-96</b>	<b>H</b>	<b>G4</b>	<b>G4</b>	<b>H</b>
<b>Spiro-97</b>	<b>H</b>	<b>G5</b>	<b>G5</b>	<b>H</b>
<b>Spiro-98</b>	<b>H</b>	<b>G6</b>	<b>G6</b>	<b>H</b>
<b>Spiro-99</b>	<b>H</b>	<b>G7</b>	<b>G7</b>	<b>H</b>

Spiro-100	H	G8	G8	H
Spiro-101	H	G9	G9	H
Spiro-102	H	G10	G10	H
Spiro-103	H	G11	G11	H
Spiro-104	H	G12	G12	H
Spiro-105	H	G13	G13	H
Spiro-106	H	G14	G14	H

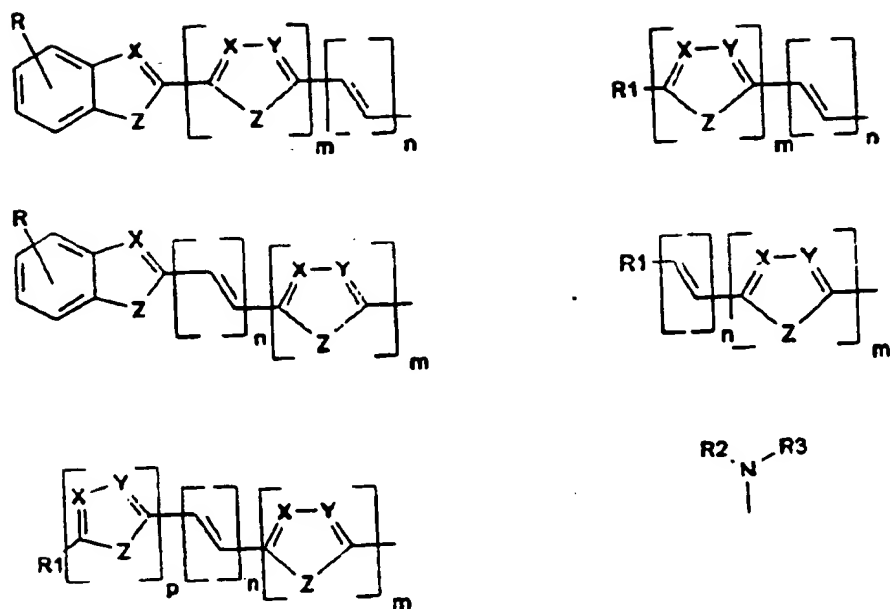
Some of the spiro compounds used in accordance with this invention are known and some are new. Thus, the subject matter of the present invention are also spiro compounds of the formula (V),



(V)

where the symbols have the following meanings:

A, B, K, L, M, N are identical or different



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and

A, B can also be identical or different and be a linear or branched alkyl, alkyloxy, or ester group with 1 to 22 C atoms, -CN, -NO<sub>2</sub>, -Ar or -O-Ar;

R is -H, a linear or branched alkyl, alkoxy, or ester group with 1 to 22, preferably 1 to 15, more preferably 1 to 12 C atoms, -CN, -NO<sub>2</sub>, -NR<sup>2</sup>R<sup>3</sup>, -Ar, or -O-Ar;

Ar is phenyl, biphenyl, 1-naphthyl, 2-naphthyl, 2-thienyl, 2-furanyl, where each of these groups may have one or two R residues,

m, n, p are 0, 1, 2, or 3;

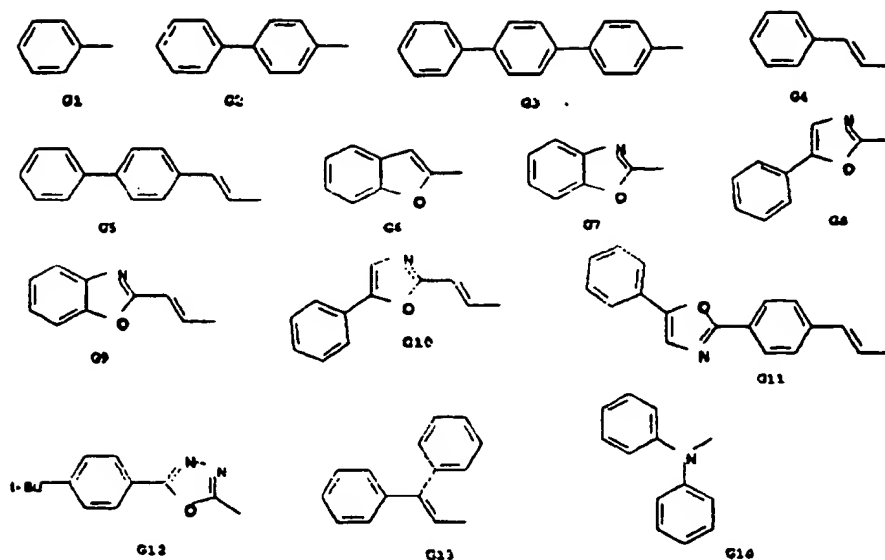
X, Y are identical or different and are CR, N;

Z is -O-, -S-, -NR<sup>1</sup>-, -CR<sup>1</sup>R<sup>4</sup>-, -CH=CH-, -CH=N-;

R<sup>1</sup>, R<sup>4</sup> are identical or different and can have the same meaning as R;

R<sup>2</sup>, R<sup>3</sup> are identical or different and are H, a linear or branched alkyl group with 1 to 22 C atoms, -Ar or 3-methylphenyl.

Preferred are compounds of the formula (V) in which K, L, M, N, and optionally A, B are selected from the following group of G1 to G14:



More preferable spiro compounds of the formula (V) are 2,2',4,4',7,7'-hexakis(biphenyl)-9,9'-spirobifluorene, 2,2',4,4',7,7'-hexakis(terphenyl)-9,9'-spirobifluorene, and the compounds listed in tables 2 and 5, where the abbreviations G1 to G14 have the same meanings as in formula (IV).

Table 2: spiro compounds of the formula (V)

/2

0

A = B = G1

Verbindung	K	L	M	N
Spiro-107	G1	G1	G3	G3
Spiro-108	G1	G1	G4	G4
Spiro-109	G1	G1	G5	G5
Spiro-110	G1	G1	G6	G6
Spiro-111	G1	G1	G7	G7
Spiro-112	G1	G1	G8	G8
Spiro-113	G1	G1	G9	G9
Spiro-114	G1	G1	G10	G10
Spiro-115	G1	G1	G11	G11
Spiro-116	G1	G1	G12	G12
Spiro-117	G1	G1	G13	G13
Spiro-118	G1	G1	G14	G14
Spiro-119	G2	G2	G2	G2
Spiro-120	G2	G2	G3	G3
Spiro-121	G2	G2	G4	G4
Spiro-122	G2	G2	G5	G5
Spiro-123	G2	G2	G6	G6
Spiro-124	G2	G2	G7	G7
Spiro-125	G2	G2	G8	G8
Spiro-126	G2	G2	G9	G9
Spiro-127	G2	G2	G10	G10
Spiro-128	G2	G2	G11	G11
Spiro-129	G2	G2	G12	G12
Spiro-130	G2	G2	G13	G13
Spiro-131	G2	G2	G14	G14

Key:

Verbindung=Compound

<b>Spiro-132</b>	<b>G3</b>	<b>G3</b>	<b>G3</b>	<b>G3</b>
<b>Spiro-133</b>	<b>G3</b>	<b>G3</b>	<b>G4</b>	<b>G4</b>
<b>Spiro-134</b>	<b>G3</b>	<b>G3</b>	<b>G5</b>	<b>G5</b>
<b>Spiro-135</b>	<b>G3</b>	<b>G3</b>	<b>G6</b>	<b>G6</b>
<b>Spiro-136</b>	<b>G3</b>	<b>G3</b>	<b>G7</b>	<b>G7</b>
<b>Spiro-137</b>	<b>G3</b>	<b>G3</b>	<b>G8</b>	<b>G8</b>
<b>Spiro-138</b>	<b>G3</b>	<b>G3</b>	<b>G9</b>	<b>G9</b>
<b>Spiro-139</b>	<b>G3</b>	<b>G3</b>	<b>G10</b>	<b>G10</b>
<b>Spiro-140</b>	<b>G3</b>	<b>G3</b>	<b>G11</b>	<b>G11</b>
<b>Spiro-141</b>	<b>G3</b>	<b>G3</b>	<b>G12</b>	<b>G12</b>
<b>Spiro-142</b>	<b>G3</b>	<b>G3</b>	<b>G13</b>	<b>G13</b>
<b>Spiro-143</b>	<b>G3</b>	<b>G3</b>	<b>G14</b>	<b>G14</b>
<b>Spiro-144</b>	<b>G4</b>	<b>G4</b>	<b>G4</b>	<b>G4</b>
<b>Spiro-145</b>	<b>G5</b>	<b>G5</b>	<b>G5</b>	<b>G5</b>
<b>Spiro-146</b>	<b>G6</b>	<b>G6</b>	<b>G6</b>	<b>G6</b>
<b>Spiro-147</b>	<b>G7</b>	<b>G7</b>	<b>G7</b>	<b>G7</b>
<b>Spiro-148</b>	<b>G8</b>	<b>G8</b>	<b>G8</b>	<b>G8</b>
<b>Spiro-149</b>	<b>G9</b>	<b>G9</b>	<b>G9</b>	<b>G9</b>
<b>Spiro-150</b>	<b>G10</b>	<b>G10</b>	<b>G10</b>	<b>G10</b>
<b>Spiro-151</b>	<b>G11</b>	<b>G11</b>	<b>G11</b>	<b>G11</b>
<b>Spiro-152</b>	<b>G12</b>	<b>G12</b>	<b>G12</b>	<b>G12</b>
<b>Spiro-153</b>	<b>G13</b>	<b>G13</b>	<b>G13</b>	<b>G13</b>
<b>Spiro-154</b>	<b>G14</b>	<b>G14</b>	<b>G14</b>	<b>G14</b>
<b>Spiro-155</b>	<b>H</b>	<b>H</b>	<b>G3</b>	<b>G3</b>
<b>Spiro-156</b>	<b>H</b>	<b>H</b>	<b>G4</b>	<b>G4</b>
<b>Spiro-157</b>	<b>H</b>	<b>H</b>	<b>G5</b>	<b>G5</b>
<b>Spiro-158</b>	<b>H</b>	<b>H</b>	<b>G6</b>	<b>G6</b>
<b>Spiro-159</b>	<b>H</b>	<b>H</b>	<b>G7</b>	<b>G7</b>



Spiro-160	H	H	G8	G8
Spiro-161	H	H	G9	G9
Spiro-162	H	H	G10	G10
Spiro-163	H	H	G11	G11
Spiro-164	H	H	G12	G12
Spiro-165	H	H	G13	G13
Spiro-166	H	H	G14	G14
Spiro-167	G1	G3	G3	G1
Spiro-168	G1	G4	G4	G1
Spiro-169	G1	G5	G5	G1
Spiro-170	G1	G6	G6	G1
Spiro-171	G1	G7	G7	G1
Spiro-172	G1	G8	G8	G1
Spiro-173	G1	G9	G9	G1
Spiro-174	G1	G10	G10	G1
Spiro-175	G1	G11	G11	G1
Spiro-176	G1	G12	G12	G1
Spiro-177	G1	G13	G13	G1
Spiro-178	G1	G14	G14	G1
Spiro-179	G2	G4	G4	G2
Spiro-180	G2	G5	G5	G2
Spiro-181	G2	G6	G6	G2
Spiro-182	G2	G7	G7	G2
Spiro-183	G2	G8	G8	G2
Spiro-184	G2	G9	G9	G2
Spiro-185	G2	G10	G10	G2
Spiro-186	G2	G11	G11	G2
Spiro-187	G2	G12	G12	G2

<b>Spiro-188</b>	<b>G2</b>	<b>G13</b>	<b>G13</b>	<b>G2</b>
<b>Spiro-189</b>	<b>G2</b>	<b>G14</b>	<b>G14</b>	<b>G2</b>
<b>Spiro-190</b>	<b>G3</b>	<b>G4</b>	<b>G4</b>	<b>G3</b>
<b>Spiro-191</b>	<b>G3</b>	<b>G5</b>	<b>G5</b>	<b>G3</b>
<b>Spiro-192</b>	<b>G3</b>	<b>G6</b>	<b>G6</b>	<b>G3</b>
<b>Spiro-193</b>	<b>G3</b>	<b>G7</b>	<b>G7</b>	<b>G3</b>
<b>Spiro-194</b>	<b>G3</b>	<b>G8</b>	<b>G8</b>	<b>G3</b>
<b>Spiro-195</b>	<b>G3</b>	<b>G9</b>	<b>G9</b>	<b>G3</b>
<b>Spiro-196</b>	<b>G3</b>	<b>G10</b>	<b>G10</b>	<b>G3</b>
<b>Spiro-197</b>	<b>G3</b>	<b>G11</b>	<b>G11</b>	<b>G3</b>
<b>Spiro-198</b>	<b>G3</b>	<b>G12</b>	<b>G12</b>	<b>G3</b>
<b>Spiro-199</b>	<b>G3</b>	<b>G13</b>	<b>G13</b>	<b>G3</b>
<b>Spiro-200</b>	<b>G3</b>	<b>G14</b>	<b>G14</b>	<b>G3</b>
<b>Spiro-201</b>	<b>H</b>	<b>G3</b>	<b>G3</b>	<b>H</b>
<b>Spiro-202</b>	<b>H</b>	<b>G4</b>	<b>G4</b>	<b>H</b>
<b>Spiro-203</b>	<b>H</b>	<b>G5</b>	<b>G5</b>	<b>H</b>
<b>Spiro-204</b>	<b>H</b>	<b>G6</b>	<b>G6</b>	<b>H</b>
<b>Spiro-205</b>	<b>H</b>	<b>G7</b>	<b>G7</b>	<b>H</b>
<b>Spiro-206</b>	<b>H</b>	<b>G8</b>	<b>G8</b>	<b>H</b>
<b>Spiro-207</b>	<b>H</b>	<b>G9</b>	<b>G9</b>	<b>H</b>
<b>Spiro-208</b>	<b>H</b>	<b>G10</b>	<b>G10</b>	<b>H</b>
<b>Spiro-209</b>	<b>H</b>	<b>G11</b>	<b>G11</b>	<b>H</b>
<b>Spiro-210</b>	<b>H</b>	<b>G12</b>	<b>G12</b>	<b>H</b>
<b>Spiro-211</b>	<b>H</b>	<b>G13</b>	<b>G13</b>	<b>H</b>
<b>Spiro-212</b>	<b>H</b>	<b>G14</b>	<b>G14</b>	<b>H</b>

Table 3: Spiro compounds of the formula (V)

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A = B = G2

Verbindung	K	L	M	N
Spiro-213	G1	G1	G3	G3
Spiro-214	G1	G1	G4	G4
Spiro-215	G1	G1	G5	G5
Spiro-216	G1	G1	G6	G6
Spiro-217	G1	G1	G7	G7
Spiro-218	G1	G1	G8	G8
Spiro-219	G1	G1	G9	G9
Spiro-220	G1	G1	G10	G10
Spiro-221	G1	G1	G11	G11
Spiro-222	G1	G1	G12	G12
Spiro-223	G1	G1	G13	G13
Spiro-224	G1	G1	G14	G14
Spiro-225	G2	G2	G2	G2
Spiro-226	G2	G2	G3	G3
Spiro-227	G2	G2	G4	G4
Spiro-228	G2	G2	G5	G5
Spiro-229	G2	G2	G6	G6
Spiro-230	G2	G2	G7	G7
Spiro-231	G2	G2	G8	G8
Spiro-232	G2	G2	G9	G9
Spiro-233	G2	G2	G10	G10
Spiro-234	G2	G2	G11	G11
Spiro-235	G2	G2	G12	G12
Spiro-236	G2	G2	G13	G13
Spiro-237	G2	G2	G14	G14

Key:

Verbindung=Compound

<b>Spiro-238</b>	<b>G3</b>	<b>G3</b>	<b>G3</b>	<b>G3</b>
<b>Spiro-239</b>	<b>G3</b>	<b>G3</b>	<b>G4</b>	<b>G4</b>
<b>Spiro-240</b>	<b>G3</b>	<b>G3</b>	<b>G5</b>	<b>G5</b>
<b>Spiro-241</b>	<b>G3</b>	<b>G3</b>	<b>G6</b>	<b>G6</b>
<b>Spiro-242</b>	<b>G3</b>	<b>G3</b>	<b>G7</b>	<b>G7</b>
<b>Spiro-243</b>	<b>G3</b>	<b>G3</b>	<b>G8</b>	<b>G8</b>
<b>Spiro-244</b>	<b>G3</b>	<b>G3</b>	<b>G9</b>	<b>G9</b>
<b>Spiro-245</b>	<b>G3</b>	<b>G3</b>	<b>G10</b>	<b>G10</b>
<b>Spiro-246</b>	<b>G3</b>	<b>G3</b>	<b>G11</b>	<b>G11</b>
<b>Spiro-247</b>	<b>G3</b>	<b>G3</b>	<b>G12</b>	<b>G12</b>
<b>Spiro-248</b>	<b>G3</b>	<b>G3</b>	<b>G13</b>	<b>G13</b>
<b>Spiro-249</b>	<b>G3</b>	<b>G3</b>	<b>G14</b>	<b>G14</b>
<b>Spiro-250</b>	<b>G4</b>	<b>G4</b>	<b>G4</b>	<b>G4</b>
<b>Spiro-251</b>	<b>G5</b>	<b>G5</b>	<b>G5</b>	<b>G5</b>
<b>Spiro-252</b>	<b>G6</b>	<b>G6</b>	<b>G6</b>	<b>G6</b>
<b>Spiro-253</b>	<b>G7</b>	<b>G7</b>	<b>G7</b>	<b>G7</b>
<b>Spiro-254</b>	<b>G8</b>	<b>G8</b>	<b>G8</b>	<b>G8</b>
<b>Spiro-255</b>	<b>G9</b>	<b>G9</b>	<b>G9</b>	<b>G9</b>
<b>Spiro-256</b>	<b>G10</b>	<b>G10</b>	<b>G10</b>	<b>G10</b>
<b>Spiro-257</b>	<b>G11</b>	<b>G11</b>	<b>G11</b>	<b>G11</b>
<b>Spiro-258</b>	<b>G12</b>	<b>G12</b>	<b>G12</b>	<b>G12</b>
<b>Spiro-259</b>	<b>G13</b>	<b>G13</b>	<b>G13</b>	<b>G13</b>
<b>Spiro-260</b>	<b>G14</b>	<b>G14</b>	<b>G14</b>	<b>G14</b>
<b>Spiro-261</b>	<b>H</b>	<b>H</b>	<b>G3</b>	<b>G3</b>
<b>Spiro-262</b>	<b>H</b>	<b>H</b>	<b>G4</b>	<b>G4</b>
<b>Spiro-263</b>	<b>H</b>	<b>H</b>	<b>G5</b>	<b>G5</b>
<b>Spiro-264</b>	<b>H</b>	<b>H</b>	<b>G6</b>	<b>G6</b>
<b>Spiro-265</b>	<b>H</b>	<b>H</b>	<b>G7</b>	<b>G7</b>

Spiro-294	G2	G13	G13	G2
Spiro-295	G2	G14	G14	G2
Spiro-296	G3	G4	G4	G3
Spiro-297	G3	G5	G5	G3
Spiro-298	G3	G6	G6	G3
Spiro-299	G3	G7	G7	G3
Spiro-300	G3	G8	G8	G3
Spiro-301	G3	G9	G9	G3
Spiro-302	G3	G10	G10	G3
Spiro-303	G3	G11	G11	G3
Spiro-304	G3	G12	G12	G3
Spiro-305	G3	G13	G13	G3
Spiro-306	G3	G14	G14	G3
Spiro-307	H	G3	G3	H
Spiro-308	H	G4	G4	H
Spiro-309	H	G5	G5	H
Spiro-310	H	G6	G6	H
Spiro-311	H	G7	G7	H
Spiro-312	H	G8	G8	H
Spiro-313	H	G9	G9	H
Spiro-314	H	G10	G10	H
Spiro-315	H	G11	G11	H
Spiro-316	H	G12	G12	H
Spiro-317	H	G13	G13	H
Spiro-318	H	G14	G14	H

Table 4: Spiro compounds of the formula (V)

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A = B = G3

Verbindung	K	L	M	N
Spiro-319	G1	G1	G3	G3
Spiro-320	G1	G1	G4	G4
Spiro-321	G1	G1	G5	G5
Spiro-322	G1	G1	G6	G6
Spiro-323	G1	G1	G7	G7
Spiro-324	G1	G1	G8	G8
Spiro-325	G1	G1	G9	G9
Spiro-326	G1	G1	G10	G10
Spiro-327	G1	G1	G11	G11
Spiro-328	G1	G1	G12	G12
Spiro-329	G1	G1	G13	G13
Spiro-330	G1	G1	G14	G14
Spiro-331	G2	G2	G2	G2
Spiro-332	G2	G2	G3	G3
Spiro-333	G2	G2	G4	G4
Spiro-334	G2	G2	G5	G5
Spiro-335	G2	G2	G6	G6
Spiro-336	G2	G2	G7	G7
Spiro-337	G2	G2	G8	G8
Spiro-338	G2	G2	G9	G9
Spiro-339	G2	G2	G10	G10
Spiro-340	G2	G2	G11	G11
Spiro-341	G2	G2	G12	G12
Spiro-342	G2	G2	G13	G13
Spiro-343	G2	G2	G14	G14

Key:

Verbindung=Compound

<b>Spiro-344</b>	<b>G3</b>	<b>G3</b>	<b>G3</b>	<b>G3</b>
<b>Spiro-345</b>	<b>G3</b>	<b>G3</b>	<b>G4</b>	<b>G4</b>
<b>Spiro-346</b>	<b>G3</b>	<b>G3</b>	<b>G5</b>	<b>G5</b>
<b>Spiro-347</b>	<b>G3</b>	<b>G3</b>	<b>G6</b>	<b>G6</b>
<b>Spiro-348</b>	<b>G3</b>	<b>G3</b>	<b>G7</b>	<b>G7</b>
<b>Spiro-349</b>	<b>G3</b>	<b>G3</b>	<b>G8</b>	<b>G8</b>
<b>Spiro-350</b>	<b>G3</b>	<b>G3</b>	<b>G9</b>	<b>G9</b>
<b>Spiro-351</b>	<b>G3</b>	<b>G3</b>	<b>G10</b>	<b>G10</b>
<b>Spiro-352</b>	<b>G3</b>	<b>G3</b>	<b>G11</b>	<b>G11</b>
<b>Spiro-353</b>	<b>G3</b>	<b>G3</b>	<b>G12</b>	<b>G12</b>
<b>Spiro-354</b>	<b>G3</b>	<b>G3</b>	<b>G13</b>	<b>G13</b>
<b>Spiro-355</b>	<b>G3</b>	<b>G3</b>	<b>G14</b>	<b>G14</b>
<b>Spiro-356</b>	<b>G4</b>	<b>G4</b>	<b>G4</b>	<b>G4</b>
<b>Spiro-357</b>	<b>G5</b>	<b>G5</b>	<b>G5</b>	<b>G5</b>
<b>Spiro-358</b>	<b>G6</b>	<b>G6</b>	<b>G6</b>	<b>G6</b>
<b>Spiro-359</b>	<b>G7</b>	<b>G7</b>	<b>G7</b>	<b>G7</b>
<b>Spiro-360</b>	<b>G8</b>	<b>G8</b>	<b>G8</b>	<b>G8</b>
<b>Spiro-361</b>	<b>G9</b>	<b>G9</b>	<b>G9</b>	<b>G9</b>
<b>Spiro-362</b>	<b>G10</b>	<b>G10</b>	<b>G10</b>	<b>G10</b>
<b>Spiro-363</b>	<b>G11</b>	<b>G11</b>	<b>G11</b>	<b>G11</b>
<b>Spiro-364</b>	<b>G12</b>	<b>G12</b>	<b>G12</b>	<b>G12</b>
<b>Spiro-365</b>	<b>G13</b>	<b>G13</b>	<b>G13</b>	<b>G13</b>
<b>Spiro-366</b>	<b>G14</b>	<b>G14</b>	<b>G14</b>	<b>G14</b>
<b>Spiro-367</b>	<b>H</b>	<b>H</b>	<b>G3</b>	<b>G3</b>
<b>Spiro-368</b>	<b>H</b>	<b>H</b>	<b>G4</b>	<b>G4</b>
<b>Spiro-369</b>	<b>H</b>	<b>H</b>	<b>G5</b>	<b>G5</b>
<b>Spiro-370</b>	<b>H</b>	<b>H</b>	<b>G6</b>	<b>G6</b>
<b>Spiro-371</b>	<b>H</b>	<b>H</b>	<b>G7</b>	<b>G7</b>

<b>Spiro-372</b>	<b>H</b>	<b>H</b>	<b>G8</b>	<b>G8</b>
<b>Spiro-373</b>	<b>H</b>	<b>H</b>	<b>G9</b>	<b>G9</b>
<b>Spiro-374</b>	<b>H</b>	<b>H</b>	<b>G10</b>	<b>G10</b>
<b>Spiro-375</b>	<b>H</b>	<b>H</b>	<b>G11</b>	<b>G11</b>
<b>Spiro-376</b>	<b>H</b>	<b>H</b>	<b>G12</b>	<b>G12</b>
<b>Spiro-377</b>	<b>H</b>	<b>H</b>	<b>G13</b>	<b>G13</b>
<b>Spiro-378</b>	<b>H</b>	<b>H</b>	<b>G14</b>	<b>G14</b>
<b>Spiro-379</b>	<b>G1</b>	<b>G3</b>	<b>G3</b>	<b>G1</b>
<b>Spiro-380</b>	<b>G1</b>	<b>G4</b>	<b>G4</b>	<b>G1</b>
<b>Spiro-381</b>	<b>G1</b>	<b>G5</b>	<b>G5</b>	<b>G1</b>
<b>Spiro-382</b>	<b>G1</b>	<b>G6</b>	<b>G6</b>	<b>G1</b>
<b>Spiro-383</b>	<b>G1</b>	<b>G7</b>	<b>G7</b>	<b>G1</b>
<b>Spiro-384</b>	<b>G1</b>	<b>G8</b>	<b>G8</b>	<b>G1</b>
<b>Spiro-385</b>	<b>G1</b>	<b>G9</b>	<b>G9</b>	<b>G1</b>
<b>Spiro-386</b>	<b>G1</b>	<b>G10</b>	<b>G10</b>	<b>G1</b>
<b>Spiro-387</b>	<b>G1</b>	<b>G11</b>	<b>G11</b>	<b>G1</b>
<b>Spiro-388</b>	<b>G1</b>	<b>G12</b>	<b>G12</b>	<b>G1</b>
<b>Spiro-389</b>	<b>G1</b>	<b>G13</b>	<b>G13</b>	<b>G1</b>
<b>Spiro-390</b>	<b>G1</b>	<b>G14</b>	<b>G14</b>	<b>G1</b>
<b>Spiro-391</b>	<b>G2</b>	<b>G4</b>	<b>G4</b>	<b>G2</b>
<b>Spiro-392</b>	<b>G2</b>	<b>G5</b>	<b>G5</b>	<b>G2</b>
<b>Spiro-393</b>	<b>G2</b>	<b>G6</b>	<b>G6</b>	<b>G2</b>
<b>Spiro-394</b>	<b>G2</b>	<b>G7</b>	<b>G7</b>	<b>G2</b>
<b>Spiro-395</b>	<b>G2</b>	<b>G8</b>	<b>G8</b>	<b>G2</b>
<b>Spiro-396</b>	<b>G2</b>	<b>G9</b>	<b>G9</b>	<b>G2</b>
<b>Spiro-397</b>	<b>G2</b>	<b>G10</b>	<b>G10</b>	<b>G2</b>
<b>Spiro-398</b>	<b>G2</b>	<b>G11</b>	<b>G11</b>	<b>G2</b>
<b>Spiro-399</b>	<b>G2</b>	<b>G12</b>	<b>G12</b>	<b>G2</b>



<b>Spiro-400</b>	<b>G2</b>	<b>G13</b>	<b>G13</b>	<b>G2</b>
<b>Spiro-401</b>	<b>G2</b>	<b>G14</b>	<b>G14</b>	<b>G2</b>
<b>Spiro-402</b>	<b>G3</b>	<b>G4</b>	<b>G4</b>	<b>G3</b>
<b>Spiro-403</b>	<b>G3</b>	<b>G5</b>	<b>G5</b>	<b>G3</b>
<b>Spiro-404</b>	<b>G3</b>	<b>G6</b>	<b>G6</b>	<b>G3</b>
<b>Spiro-405</b>	<b>G3</b>	<b>G7</b>	<b>G7</b>	<b>G3</b>
<b>Spiro-406</b>	<b>G3</b>	<b>G8</b>	<b>G8</b>	<b>G3</b>
<b>Spiro-407</b>	<b>G3</b>	<b>G9</b>	<b>G9</b>	<b>G3</b>
<b>Spiro-408</b>	<b>G3</b>	<b>G10</b>	<b>G10</b>	<b>G3</b>
<b>Spiro-409</b>	<b>G3</b>	<b>G11</b>	<b>G11</b>	<b>G3</b>
<b>Spiro-410</b>	<b>G3</b>	<b>G12</b>	<b>G12</b>	<b>G3</b>
<b>Spiro-411</b>	<b>G3</b>	<b>G13</b>	<b>G13</b>	<b>G3</b>
<b>Spiro-412</b>	<b>G3</b>	<b>G14</b>	<b>G14</b>	<b>G3</b>
<b>Spiro-413</b>	<b>H</b>	<b>G3</b>	<b>G3</b>	<b>H</b>
<b>Spiro-414</b>	<b>H</b>	<b>G4</b>	<b>G4</b>	<b>H</b>
<b>Spiro-415</b>	<b>H</b>	<b>G5</b>	<b>G5</b>	<b>H</b>
<b>Spiro-416</b>	<b>H</b>	<b>G6</b>	<b>G6</b>	<b>H</b>
<b>Spiro-417</b>	<b>H</b>	<b>G7</b>	<b>G7</b>	<b>H</b>
<b>Spiro-418</b>	<b>H</b>	<b>G8</b>	<b>G8</b>	<b>H</b>
<b>Spiro-419</b>	<b>H</b>	<b>G9</b>	<b>G9</b>	<b>H</b>
<b>Spiro-420</b>	<b>H</b>	<b>G10</b>	<b>G10</b>	<b>H</b>
<b>Spiro-421</b>	<b>H</b>	<b>G11</b>	<b>G11</b>	<b>H</b>
<b>Spiro-422</b>	<b>H</b>	<b>G12</b>	<b>G12</b>	<b>H</b>
<b>Spiro-423</b>	<b>H</b>	<b>G13</b>	<b>G13</b>	<b>H</b>
<b>Spiro-424</b>	<b>H</b>	<b>G14</b>	<b>G14</b>	<b>H</b>

Table 5: Spiro compounds of the formula (V)

/3

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A = B = G12

Verbindung	K	L	M	N
Spiro-425	G1	G1	G3	G3
Spiro-426	G1	G1	G4	G4
Spiro-427	G1	G1	G5	G5
Spiro-428	G1	G1	G6	G6
Spiro-429	G1	G1	G7	G7
Spiro-430	G1	G1	G8	G8
Spiro-431	G1	G1	G9	G9
Spiro-432	G1	G1	G10	G10
Spiro-433	G1	G1	G11	G11
Spiro-434	G1	G1	G12	G12
Spiro-435	G1	G1	G13	G13
Spiro-436	G1	G1	G14	G14
Spiro-437	G2	G2	G2	G2
Spiro-438	G2	G2	G3	G3
Spiro-439	G2	G2	G4	G4
Spiro-440	G2	G2	G5	G5
Spiro-441	G2	G2	G6	G6
Spiro-442	G2	G2	G7	G7
Spiro-443	G2	G2	G8	G8
Spiro-444	G2	G2	G9	G9
Spiro-445	G2	G2	G10	G10
Spiro-446	G2	G2	G11	G11
Spiro-447	G2	G2	G12	G12
Spiro-448	G2	G2	G13	G13
Spiro-449	G2	G2	G14	G14

Key:

Verbindung=Compound

<b>Spiro-450</b>	<b>G3</b>	<b>G3</b>	<b>G3</b>	<b>G3</b>
<b>Spiro-451</b>	<b>G3</b>	<b>G3</b>	<b>G4</b>	<b>G4</b>
<b>Spiro-452</b>	<b>G3</b>	<b>G3</b>	<b>G5</b>	<b>G5</b>
<b>Spiro-453</b>	<b>G3</b>	<b>G3</b>	<b>G6</b>	<b>G6</b>
<b>Spiro-454</b>	<b>G3</b>	<b>G3</b>	<b>G7</b>	<b>G7</b>
<b>Spiro-455</b>	<b>G3</b>	<b>G3</b>	<b>G8</b>	<b>G8</b>
<b>Spiro-456</b>	<b>G3</b>	<b>G3</b>	<b>G9</b>	<b>G9</b>
<b>Spiro-457</b>	<b>G3</b>	<b>G3</b>	<b>G10</b>	<b>G10</b>
<b>Spiro-458</b>	<b>G3</b>	<b>G3</b>	<b>G11</b>	<b>G11</b>
<b>Spiro-459</b>	<b>G3</b>	<b>G3</b>	<b>G12</b>	<b>G12</b>
<b>Spiro-460</b>	<b>G3</b>	<b>G3</b>	<b>G13</b>	<b>G13</b>
<b>Spiro-461</b>	<b>G3</b>	<b>G3</b>	<b>G14</b>	<b>G14</b>
<b>Spiro-462</b>	<b>G4</b>	<b>G4</b>	<b>G4</b>	<b>G4</b>
<b>Spiro-463</b>	<b>G5</b>	<b>G5</b>	<b>G5</b>	<b>G5</b>
<b>Spiro-464</b>	<b>G6</b>	<b>G6</b>	<b>G6</b>	<b>G6</b>
<b>Spiro-465</b>	<b>G7</b>	<b>G7</b>	<b>G7</b>	<b>G7</b>
<b>Spiro-466</b>	<b>G8</b>	<b>G8</b>	<b>G8</b>	<b>G8</b>
<b>Spiro-467</b>	<b>G9</b>	<b>G9</b>	<b>G9</b>	<b>G9</b>
<b>Spiro-468</b>	<b>G10</b>	<b>G10</b>	<b>G10</b>	<b>G10</b>
<b>Spiro-469</b>	<b>G11</b>	<b>G11</b>	<b>G11</b>	<b>G11</b>
<b>Spiro-470</b>	<b>G12</b>	<b>G12</b>	<b>G12</b>	<b>G12</b>
<b>Spiro-471</b>	<b>G13</b>	<b>G13</b>	<b>G13</b>	<b>G13</b>
<b>Spiro-472</b>	<b>G14</b>	<b>G14</b>	<b>G14</b>	<b>G14</b>
<b>Spiro-473</b>	<b>H</b>	<b>H</b>	<b>G3</b>	<b>G3</b>
<b>Spiro-474</b>	<b>H</b>	<b>H</b>	<b>G4</b>	<b>G4</b>
<b>Spiro-475</b>	<b>H</b>	<b>H</b>	<b>G5</b>	<b>G5</b>
<b>Spiro-476</b>	<b>H</b>	<b>H</b>	<b>G6</b>	<b>G6</b>
<b>Spiro-477</b>	<b>H</b>	<b>H</b>	<b>G7</b>	<b>G7</b>

<b>Spiro-478</b>	<b>H</b>	<b>H</b>	<b>G8</b>	<b>G8</b>
<b>Spiro-479</b>	<b>H</b>	<b>H</b>	<b>G9</b>	<b>G9</b>
<b>Spiro-480</b>	<b>H</b>	<b>H</b>	<b>G10</b>	<b>G10</b>
<b>Spiro-481</b>	<b>H</b>	<b>H</b>	<b>G11</b>	<b>G11</b>
<b>Spiro-482</b>	<b>H</b>	<b>H</b>	<b>G12</b>	<b>G12</b>
<b>Spiro-483</b>	<b>H</b>	<b>H</b>	<b>G13</b>	<b>G13</b>
<b>Spiro-484</b>	<b>H</b>	<b>H</b>	<b>G14</b>	<b>G14</b>
<b>Spiro-485</b>	<b>G1</b>	<b>G3</b>	<b>G3</b>	<b>G1</b>
<b>Spiro-486</b>	<b>G1</b>	<b>G4</b>	<b>G4</b>	<b>G1</b>
<b>Spiro-487</b>	<b>G1</b>	<b>G5</b>	<b>G5</b>	<b>G1</b>
<b>Spiro-488</b>	<b>G1</b>	<b>G6</b>	<b>G6</b>	<b>G1</b>
<b>Spiro-489</b>	<b>G1</b>	<b>G7</b>	<b>G7</b>	<b>G1</b>
<b>Spiro-490</b>	<b>G1</b>	<b>G8</b>	<b>G8</b>	<b>G1</b>
<b>Spiro-491</b>	<b>G1</b>	<b>G9</b>	<b>G9</b>	<b>G1</b>
<b>Spiro-492</b>	<b>G1</b>	<b>G10</b>	<b>G10</b>	<b>G1</b>
<b>Spiro-493</b>	<b>G1</b>	<b>G11</b>	<b>G11</b>	<b>G1</b>
<b>Spiro-494</b>	<b>G1</b>	<b>G12</b>	<b>G12</b>	<b>G1</b>
<b>Spiro-495</b>	<b>G1</b>	<b>G13</b>	<b>G13</b>	<b>G1</b>
<b>Spiro-496</b>	<b>G1</b>	<b>G14</b>	<b>G14</b>	<b>G1</b>
<b>Spiro-497</b>	<b>G2</b>	<b>G4</b>	<b>G4</b>	<b>G2</b>
<b>Spiro-498</b>	<b>G2</b>	<b>G5</b>	<b>G5</b>	<b>G2</b>
<b>Spiro-499</b>	<b>G2</b>	<b>G6</b>	<b>G6</b>	<b>G2</b>
<b>Spiro-500</b>	<b>G2</b>	<b>G7</b>	<b>G7</b>	<b>G2</b>
<b>Spiro-501</b>	<b>G2</b>	<b>G8</b>	<b>G8</b>	<b>G2</b>
<b>Spiro-502</b>	<b>G2</b>	<b>G9</b>	<b>G9</b>	<b>G2</b>
<b>Spiro-503</b>	<b>G2</b>	<b>G10</b>	<b>G10</b>	<b>G2</b>
<b>Spiro-504</b>	<b>G2</b>	<b>G11</b>	<b>G11</b>	<b>G2</b>
<b>Spiro-505</b>	<b>G2</b>	<b>G12</b>	<b>G12</b>	<b>G2</b>

<b>Spiro-506</b>	<b>G2</b>	<b>G13</b>	<b>G13</b>	<b>G2</b>
<b>Spiro-507</b>	<b>G2</b>	<b>G14</b>	<b>G14</b>	<b>G2</b>
<b>Spiro-508</b>	<b>G3</b>	<b>G4</b>	<b>G4</b>	<b>G3</b>
<b>Spiro-509</b>	<b>G3</b>	<b>G5</b>	<b>G5</b>	<b>G3</b>
<b>Spiro-510</b>	<b>G3</b>	<b>G6</b>	<b>G6</b>	<b>G3</b>
<b>Spiro-511</b>	<b>G3</b>	<b>G7</b>	<b>G7</b>	<b>G3</b>
<b>Spiro-512</b>	<b>G3</b>	<b>G8</b>	<b>G8</b>	<b>G3</b>
<b>Spiro-513</b>	<b>G3</b>	<b>G9</b>	<b>G9</b>	<b>G3</b>
<b>Spiro-514</b>	<b>G3</b>	<b>G10</b>	<b>G10</b>	<b>G3</b>
<b>Spiro-515</b>	<b>G3</b>	<b>G11</b>	<b>G11</b>	<b>G3</b>
<b>Spiro-516</b>	<b>G3</b>	<b>G12</b>	<b>G12</b>	<b>G3</b>
<b>Spiro-517</b>	<b>G3</b>	<b>G13</b>	<b>G13</b>	<b>G3</b>
<b>Spiro-518</b>	<b>G3</b>	<b>G14</b>	<b>G14</b>	<b>G3</b>
<b>Spiro-519</b>	<b>H</b>	<b>G3</b>	<b>G3</b>	<b>H</b>
<b>Spiro-520</b>	<b>H</b>	<b>G4</b>	<b>G4</b>	<b>H</b>
<b>Spiro-521</b>	<b>H</b>	<b>G5</b>	<b>G5</b>	<b>H</b>
<b>Spiro-522</b>	<b>H</b>	<b>G6</b>	<b>G6</b>	<b>H</b>
<b>Spiro-523</b>	<b>H</b>	<b>G7</b>	<b>G7</b>	<b>H</b>
<b>Spiro-524</b>	<b>H</b>	<b>G8</b>	<b>G8</b>	<b>H</b>
<b>Spiro-525</b>	<b>H</b>	<b>G9</b>	<b>G9</b>	<b>H</b>
<b>Spiro-526</b>	<b>H</b>	<b>G10</b>	<b>G10</b>	<b>H</b>
<b>Spiro-527</b>	<b>H</b>	<b>G11</b>	<b>G11</b>	<b>H</b>
<b>Spiro-528</b>	<b>H</b>	<b>G12</b>	<b>G12</b>	<b>H</b>
<b>Spiro-529</b>	<b>H</b>	<b>G13</b>	<b>G13</b>	<b>H</b>
<b>Spiro-530</b>	<b>H</b>	<b>G14</b>	<b>G14</b>	<b>H</b>

The spiro compounds made in accordance with this invention are prepared by conventional methods found in the literature, as described in the standard works on organic synthesis, e.g. Houben-Weyl, Methoden der Organischen Chemie [Methods of Organic Chemistry], Georg-Thieme-Verlag, Stuttgart and in the pertinent volumes of the series "The Chemistry of Heterocyclic Compounds," by A. Weissberger and E. C. Taylor (publ.).

Preparation occurs under the reaction conditions that are known and suitable for the above-mentioned reactions. Conventional variations, not mentioned here, can also be used.

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Compounds of the formula (III) are obtained, for example, from 9,9'-spirobifluorene, the synthesis of which is described, for example, by R. G. Clarkson, M. Gomberg, J. Am. Chem. Soc. 52 (1930) 2881.

Compounds of the formula (IIIa) can be prepared, for example, based on a tetrahalogenation at positions 2,2',7,7' of 9,9'-spirobifluorene and a subsequent substitution reaction (see, for example, US 5,026,894) or by tetraacetylation of positions 2,2',7,7' of 9,9'-spirobifluorene, with subsequent C-C-linkage after conversion of the acetyl groups into aldehyde groups or heterocycle formation after conversion of the acetyl groups into carboxylic acid groups.

Compounds of the formula (IIIb) can be prepared, for example, in a manner similar to those of the formula IIIa, where the stoichiometric ratios in the conversion are selected such that positions 2,2' and 7,7' are functionalized (see, for example, J. H. Weisburger, E. K. Weisburger, F. E. Ray, J. Am. Chem. Soc. 72 (1959) 4253; F. K. Sutcliffe, H. M. Shahidi, D. Paterson, J. Soc. Dyers Colour 94 (1978) 306 and G. Haas, V. Prelog, 'Helv. Chim. Acta 52 (1969) 1202).

Compounds of the formula (IIIc) can be prepared, for example, by dibromination at the 2,2' positions and subsequent diacetylation at the 7,7' positions of 9,9'-spirobifluorene, with subsequent conversion similar to that of compounds IIIa.

Compounds of the formulas (IIIe)-(IIIg) can be prepared, for example, by the choice of suitably substituted starting compounds in the structure of the spirobifluorene, e.g. 2,7-dibromospirobifluorene can be made of 2,7-dibromofluorenone and 2,7-dicarbethoxy-9,9'-spirobifluorene by the use of 2,7-dicarbethoxyfluorenone. The free 2,'7' positions of spirobifluorene can then be further substituted independently.

For the synthesis of groups K, L, M, N see, for example:

DE-A 23 44 732, 24 50 088, 24 29 093, 25 02 904, 26 36 684, 27 01 591, and 27 52 975 for compounds with 1,4-phenylene groups;

DE-A 26 41 724 for compounds with pyrimidine-2,5-diyl groups;

DE-A 40 26 223 and EP-A 03 91 203 for compounds with pyridine-2,5-diyl groups;

DE-A 32 31 462 for compounds with pyridazine-3,6-diyl groups; N.

Miyaura, T. Yanagi, and A. Suzuki in Synthetic Communications 11 (1981) 513 to 519,

DE-A-3 930 663, M. J. Sharp, W. Cheng, V. Snieckus in Tetrahedron Letters 28 (1987), 5093; G. W. Gray in J. Chem. Soc. Perkin Trans II

(1989) 2041 and Mol. Cryst. Liq. Cryst. 172 (1989) 165, Mol. Cryst. Liq. Cryst. 204 (1991) 43 and 91; EP-A 0 449 015; WO 89/12039; WO 89/03821; EP-A 0 354 434 for the direct linkage of aromatics and heteroaromatics;

The preparation of disubstituted pyridines, disubstituted pyrazines, disubstituted pyrimidines, and disubstituted pyridazines may be found, for example, in the appropriate volumes of the series "The Chemistry of Heterocyclic Compounds," by A. Weissberger and E. C. Taylor (publ.).

In accordance with this invention, the spiro compounds of the formulas (I), (II) and (III) described above are used as electroluminescent materials, i.e. they serve as the active layer in an electroluminescence device. An active layer for the purposes of this invention has electroluminescent materials that are capable of radiating light (light-emitting layer) when an electric field is applied, as well as materials that improved the injection and/or transport of positive and/or negative charges (charge-injection layers and charge transport layers).

Electroluminescent materials in accordance with this invention are also characterized, among other things, by exceptional temperature stability, compared to known organic electroluminescent materials. This is made manifest, for example, in that the emission maximum of the compounds after thermal load drops only slightly, in other cases not at all, and that in many compounds an increase in emission maximum has even been found after thermal load.

Thus, the subject matter of the present invention also an organic electroluminescent material, characterized in that its emission maximum in the region of 400 to 750 nm, measured at room temperature, is reduced by no more than 15%, relative to the initial state, after the material, applied at a thickness of no more than 1  $\mu\text{m}$  on a quartz substrate, is heated to 250°C for 30 min in an inert atmosphere at a pressure of no more than 1 mbar.

Preferably, the reduction in emission maximum is no more than 10%, more preferably 5%, relative to the initial state before thermal treatment.

More preferable are electroluminescent materials that have no reduction in emission maximum under the above-mentioned conditions.

Most preferable are those organic electroluminescent materials that show an increase in their emission maximum under the above-mentioned conditions.

"Inert atmosphere" preferably refers to a nitrogen or argon atmosphere.

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Thus, the subject matter of the present invention is also an electroluminescence device with one or more active layers that contain one or more compounds of the formula (I), (II), and/or (III). The active layer can be, for example, a light-emitting layer and/or a transport layer and/or a charge-injection layer.

The general structure of such electroluminescence devices is described, for example, in US 4,539,507 and US 5,151,629.

They typically contain an electroluminescent layer between a cathode and an anode, whereby at least one of the electrodes is transparent. Moreover, between the electroluminescent layer and the cathode an electron-injection and/or electron-transport layer can be inserted and/or between the electroluminescent layer and the anode a hole-injection and/or hole-transport layer can be placed. Ca, Mg, Al, In, Mg/Ag, for example, may serve as the cathode. Au or ITO (indium oxide/tin oxide on a transparent substrate, e.g. of glass or a transparent polymer), for example, may serve as the anode.

In operation, the cathode is set at a negative potential with respect to the anode, so that electrons from the cathode are injected into the electron-injection layer /electron-transport layer or directly into the light-emitting layer. At the same time, holes from the anode are injected into the hole-injection layer/hole-transport layer or directly into the light-emitting layer.

The injected charge carriers move through the active layers toward each other under the influence of the applied voltage. At the interface between charge-transport layer and light-emitting layer or within the light-emitting layer, this creates electron/hole pairs, which recombine while emitting light. The color of the emitted light can be varied by the compound that is used as the light-emitting layer.

Electroluminescence devices are used, for example, as self-luminescent display elements, such as control lamps, alphanumeric displays, information signs, and in optoelectronic couplers.

The invention will be explained in greater detail by the examples, without being limited by them.

#### Examples

##### A. starting compounds

##### a) Synthesis of 9,9'-spirobifluorene



6.3 g magnesium turnings and 50 mg anthracene are placed in 120 ml dry diethyl ether in a 1-liter three-necked flask with reflux condenser under argon and the magnesium is activated with ultrasound for 15 min.

62 g 2-bromobiphenyl is dissolved in 60 ml dry diethyl ether. About 10 ml of this solution is added to the prepared magnesium, in order to start the Grignard reaction.

After the reaction begins, the 2-bromobiphenyl solution is added dropwise with additional ultrasound treatment in such a way that the solution gently boils under reflux. After the material has been added, the reaction mixture is boiled for an additional hour under reflux with ultrasound.

48.8 g 9-fluorenone is dissolved in 400 ml dry diethyl ether and the Grignard solution is added dropwise under additional ultrasound treatment. After all the material has been added, it is boiled an additional 2 h. The yellow magnesium complex of 9-(2-biphenyl)-9-fluorenol that precipitates out after cooling of the reaction mixture is filtered off with suction and washed with a little ether. The magnesium complex is hydrolyzed in 800 ml ice water, which contains 40 g ammonium chloride. After stirring for 60 minutes, the 9-(2-biphenyl)-9-fluorenol that is formed is filtered off with suction, washed with water, and suctioned dry.

The dried 9-(2-biphenyl)-9-fluorenol is then dissolved hot in 500 ml glacial acetic acid. To this solution is added 0.5 ml concentrated hydrochloric acid. The solution is allowed to boil for several minutes and the 9,9'-spirobifluorene that is formed is precipitated out of the hot solution with water (water added until the solution starts to become turbid). After cooling, the product is filtered off with suction and washed with water. The dried product is recrystallized from ethanol for further purification. The yield is 66 g (80%, with reference to 2-bromobiphenyl) 9,9'-spirobifluorene, as colorless crystals, m.p. 198°C.

b) 2,2'-dibromo-9,9'-spirobifluorene

(F. K. Sutcliffe, H. M. Shahidi, D. Patterson, J. Soc. Dyers & Colourists 94 (1978) 306)

3.26 g (10.3 mmol) 9,9'-spirobifluorene is dissolved in 30 ml methylene chloride and 5 mg  $\text{FeCl}_3$  (anhydrous) is added as a catalyst. The reaction flask is protected from light. 1.12 ml (21.8 mmol) bromine in 5 ml methylene chloride is added dropwise within a period of 30 min with stirring. After 24 h the resulting brown solution is washed with saturated aqueous  $\text{NaHCO}_3$  solution and water to remove excess bromine. After drying, the organic phase is concentrated by evaporation over  $\text{Na}_2\text{SO}_4$  in a rotary evaporator. The white residue is recrystallized from methanol, yielding 3.45 g (70%) of the dibromo compound as colorless crystals, m.p.  $240^\circ\text{C}$ .

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c) 2,2',7,7'-tetrabromo-9,9'-spirobifluorene

80 mg (0.5 mmol) anhydrous  $\text{FeCl}_3$  and 2.1 ml (41 mmol) bromine in 5 ml methylene chloride are added dropwise over the course of 10 min to a solution of 3.16 g (10.0 mmol) 9,9'-spirobifluorene in 30 ml methylene chloride. The solution is boiled 6 h under reflux. Upon cooling, the product precipitates out. The precipitate is filtered off with suction and washed with a little cold methylene chloride. After drying, the yield is 6.0 g

(95%) of the tetrabromo compound as a white solid.

d) 2-Bromo-9,9'-spirobifluorene and 2,2',7-tribromo-9,9'-spirobifluorene are prepared in a similar manner using different stoichiometry.

e) 9,9'-spirobifluorene-2,2'-dicarboxylic acid

from 2,2'-dibromo-9,9'-spirobifluorene via 2,2'-Dicyano-9,9'-spirobifluorene

1.19 g 2,2'-dibromo-9,9'-spirobifluorene and 0.54 g  $\text{CuCN}$  are heated in 5 ml DMF for 6 h under reflux. The resulting brown mixture is poured into a mixture of 3 g  $\text{FeCl}_3$  (hydrat.) and 1.5 ml concentrated hydrochloric acid in 20 ml water. The mixture is held for 30 min at  $60$  to  $70^\circ\text{C}$ , in order to break down the Cu complex. The hot aqueous solution is twice extracted with toluene. The organic phases are then washed with dilute hydrochloric acid, water, and 10% aqueous  $\text{NaOH}$ . The organic phase is filtered and concentrated by evaporation. The resulting yellow residue

is recrystallized from methanol. The yield is 0.72 g (80%) 2,2'-dicyano-9,9'-spirobifluorene as pale yellowish crystals (melting range 215 to 245°C).

3 g 2,2'-dicyano-9,9'-spirobifluorene is heated under reflux with 25 ml 30% aqueous NaOH and 30 ml ethanol for 6 h. The disodium salt of spirobifluorene dicarboxylic acid precipitates out as a yellow precipitate, which is filtered off and heated in 25% aqueous HCl, in order to obtain the free acid. The spirobifluorene dicarboxylic acid is recrystallized from glacial acetic acid. The yield is 2.2 g (66.6%) white crystals (m.p. 376°C, IR band  $1,685\text{ cm}^{-1}$  C=O).

9,9'-spirobifluorene-2,2',7,7'-tetracarboxylic acid is prepared from 2,2',7,7'-tetrabromo-9,9'-spirobifluorene in a similar manner.

f) 9,9'-spirobifluorene-2,2'-dicarboxylic acid

from 9,9'-spirobifluorene via 2,2'-diacetyl-9,9'-spirobifluorene (G. Haas, V. Prelog, *Helv. Chim. Acta* 52 (1969) 1,202; V. Prelog, D. Bedekovic, *Helv. Chim. Acta* 62 (1979) 2,285). After adding 9.0 g finely powdered, anhydrous  $\text{AlCl}_3$ , a solution of 3.17 g 9,9'-spirobifluorene in 30 ml absolute carbon disulfide has added to it dropwise for 10 min with stirring 1.58 g acetyl chloride in 5 ml absolute carbon disulfide and the result is boiled for 1 hour under reflux. The mixture is evaporated under reduced pressure until dry and 100 g ice and 50 ml 2n hydrochloric acid are added at 0°C. After normal processing, the raw material is separated chromatographically with benzene/acetic ester (10:1) over silica gel.

The result is 3.62 g (89%) 2,2'-diacetyl-9,9'-spirobifluorene (recrystallized from chloroform/acetic ester, m.p. 255 to 257°C) and 204 mg 2-acetyl-9,9'-spirobifluorene (recrystallized from chloroform/benzene, m.p. 225°C).

[In addition, chromatography may also isolate 2,2',7-triacetyl-9,9'-spirobifluorene (m.p. 258 to 260°C) and 2,2',7,7'-tetraacetyl-9,9'-spirobifluorene (m.p. > 300°C), recrystallized from acetic ester/hexane].

2,2',7-Triacetyl- and 2,2',7,7'-tetraacetyl-9,9'-spirobifluorene can be obtained as the main product, using different stoichiometry.

First 7.2 g bromine and then a solution of 3.0 g 2,2'-diacetyl-9,9'-spirobifluorene in a little dioxane are added dropwise at 0°C with stirring to a solution of 6.0 g sodium hydroxide in 30 ml water. After an additional 1 hour of stirring at room temperature, 1 g sodium hydrogen sulfite dissolved in 20 ml water is added to the clear yellow solution.

After acidification with concentrated hydrochloric acid, the colorless precipitated product is filtered off and washed with a little water. Recrystallization from ethanol yields 9,9'-spirobifluorene-2,2'-dicarboxylic acid as water-clear prisms (m.p. 352°C).

9,9'-Spirobifluorene-2-carboxylic acid, 9,9'-spirobifluorene-2,2',7-tricarboxylic acid, and 9,9'-spirobifluorene-2,2',7,7'-tetracarboxylic acid are prepared in a similar manner.

g) 2,2'-bis(bromomethyl)-9,9'-spirobifluorene  
from 2,2'-dicarboxy-9,9'-spirobifluorene via 9,9'-spirobifluorene-2,2'-dimethanol

(V. Prelog, D. Bedekovicc, *Helv. Chim. Acta* 62 (1979) 2285)

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10 g of a 70 wt% solution of sodium-dihydro-bis(2-methoxyethoxy)-aluminate (Fluka) in benzene was slowly added dropwise at room temperature to a suspension of 2.0 g 2,2'-dicarboxy-9,9'-spirobifluorene (free carboxylic acid) in 20 ml benzene. After boiling for 2 h under reflux, during which time the carboxylic acid dissolves, the excess reducing agent is broken down with water at 10°C, the mixture is acidified with concentrated hydrochloric acid and extracted by shaking with chloroform.

The organic phase, which is washed with water and dried over magnesium sulfate, is concentrated by evaporation and the residue recrystallized from benzene. The yield is 1.57 g 9,9'-spirobifluorene-2,2'-dimethanol (m.p. 254 to 255°C).

91.5 g of a 33% aqueous solution of hydrogen bromide in glacial acetic acid is added dropwise to a solution of 13.5 g 9,9'-spirobifluorene-2,2'-dimethanol in 400 ml benzene and the mixture is boiled under reflux for 7 h. Then 200 ml water is added and the organic phase, which is washed with water and dried over magnesium sulfate, is concentrated by evaporation. Chromatography over silica gel with benzene yields 11.7 g 2,2'-bis(bromomethyl)-9,9'-spirobifluorene as colorless platelets (m.p. 175 to 177°C).

h) 5 g chromium(VI)oxide on graphite (Seloxcette, Alpha Inorganics) is added to a solution of 380 mg 9,9'-spirobifluorene-2,2'-dimethanol in 15 ml toluene and boiled under reflux under nitrogen for 48 h. It is then suction-filtered through a glass suction filter and the filtrate is concentrated by evaporation. Chromatography over silica gel with chloroform and crystallization from methylene chloride/ether yields 152 mg 9,9'-spirobifluorene-2,2'-dicarbaldehyd (m.p. > 300°C) and 204 mg 2'-hydroxymethyl-9,9'-spirobifluorene-2-carbaldehyde

(m.p. 262 to 263°C).

i) 2,2'-Diamino-9,9'-spirobifluorene

A mixture of 150 ml concentrated aqueous  $\text{HNO}_3$  and 150 ml glacial acetic acid is added dropwise to a boiling solution of 15.1 g 9,9'-spirobifluorene in 500 ml glacial acetic acid over a period of 30 min, after which the solution is refluxed an additional 75 min. After the solution cools and stands for 1 h, an equal volume of water is added and the product precipitates out. After filtration with suction, 18.5 g yellow crystals (m.p. 220 to 224°C) of 2,2'-dinitro-9,9'-spirobifluorene are obtained. Recrystallization from 250 ml glacial acetic acid yields 12.7 g bright yellow crystalline needles (m.p. 245 to 249°C, analytically pure 249 to 250°C).

A mixture of 4.0 ml dinitro-spirobifluorene and 4.0 g iron powder is heated under reflux in 100 ml ethanol, while 15 ml concentrated  $\text{HCl}$  is added dropwise over a period of 30 min. After an additional 30 min of boiling under reflux, the excess iron is filtered off. The green filtrate is added to a solution of 400 ml water, 15 ml concentrated  $\text{NH}_4\text{OH}$ , and 20 g Na,K-tartrate. The white diamine is filtered from the dark green solution of the iron complex. The diamine is dissolved in dilute  $\text{HCl}$  for purification and stirred and filtered at room temperature with activated carbon (Darco). The filtered solution is neutralized dropwise with  $\text{NH}_4\text{OH}$  with stirring (KPG stirrer) and the precipitated product is filtered off with suction. The yield is 3.5 g white 2,2'-diamino-9,9'-spirobifluorene, which can be recrystallized from ethanol

(m.p. 243°C).

j) Synthesis of 2,2',7,7'-tetrabromo-9,9'-spirobifluorene by bromination of solid 9,9'-spirobifluorene with bromine vapor.

3.16 g (10 mmol) finely powdered 9,9'-spirobifluorene is added to a flat porcelain evaporating dish ( $\phi$  ca. 15 cm). This dish is placed in a desiccator ( $\phi$  ca. 30 cm), on the perforated intermediate plate. On the bottom of the desiccator is 15.6 g (4.8 ml, 96 mmol) bromine in a crystallizing dish. The desiccator is closed, but with the ventilation cock open, so that the  $\text{HBr}$  that is formed can escape. The desiccator is placed under the fume hood overnight. On the next day, the porcelain dish with the product, colored orange by the bromine, is removed from the desiccator and allowed to stand under the fume hood for at least 4 h, so that any excess bromine and  $\text{HBr}$  can escape.

The product is dissolved in 150 ml dichloromethane and washed until colorless with 50 ml each of sodium sulfite solution (saturated), sodium hydrogen carbonate solution (saturated), and water. The dichloromethane

solution is dried over sodium sulfate and evaporated on a rotary evaporator. It is recrystallized from dichloromethane/pentane 4:1 for purification. Yield 5.7 g (92%) colorless crystals.

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ , ppm): 6.83 (d,  $J = 1.83$  Hz, 4 H, H-1,1',8,8'); 7.54 (dd,  $J = 7.93, 1.83$  Hz, 4 H, H-3,3',6,6'); 7.68 (d,  $J = 7.93$  Hz, 4 H, H-4,4',5,5').

#### k) Synthesis of 2,2',4,4',7,7'-hexabromo-9,9'-spirobifluorene

200 mg anhydrous  $\text{FeCl}_3$  is added to a solution of 3.16 g (10 mmol) 9,9'-spirobifluorene in 20 ml methylene chloride and treated with ultrasound. The reaction flask is protected from light with Al foil. Then, in boiling heat, 9.85 g (3.15 ml, 62 mmol) bromine in 5 ml methylene chloride is added dropwise within a period of 15 min. The solution is boiled an additional 20 h under reflux and treated with ultrasound. After cooling, petroleum ether is added and the

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mixture is filtered with suction. For further purification, it is recrystallized from THF/methanol and dried for 5 h at  $80^\circ\text{C}$ . Yield 6.15 g (77%) colorless crystals.

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ , ppm): 6.76 (d,  $J = 1.53$  Hz, 2 H, H-1,1'); 6.84 (d,  $J = 1.83$  Hz, 2 H, H-8,8'); 7.60 (dd,  $J = 8.54, 1.83$  Hz, 2 H, H-6,6'); 7.75 (d,  $J = 1.53$  Hz, 2 H, H-3,3'); 8.49 (d,  $J = 8.54$  Hz, 2 H, H-5,5').

#### l) Synthesis of 2,7-dibromo-9,9'-spirobifluorene

The Grignard reagent, prepared from 0.72 g (30 mmol) magnesium turnings and 5.1 ml (30 mmol) 2-bromobiphenyl in 15 ml diethyl ether, is added dropwise over the course of 2 h with stirring (in an ultrasonic bath) to a boiling suspension of 10.0 g (29.6 mmol) 2,7-dibromo-9-fluorenone in 100 ml dry diethyl ether. After all the material has been added, it is boiled an additional 3 h. After cooling overnight, the precipitate is filtered off with suction and washed with cold ether. The magnesium complex that has been filtered off with suction is hydrolyzed in a solution of 15 g ammonium chloride in 250 ml ice water. After 1 h the 9-(2-biphenyl)-2,7-dibromo-9-fluorenol that has formed is filtered off with suction, washed with water, and suctioned dry. For the ring-closure reaction, the dried fluorenol is boiled in 100 ml glacial acetic acid for 6 hours after 3 drops concentrated HCl have been added. The result is allowed to crystallize overnight, the product that has formed is filtered off with suction, and it is washed with glacial acetic acid and water.

Yield: 11 g (77%) 2,7-dibromo-9,9'-spirobifluorene. For additional purification, it can be recrystallized from THF.

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ , ppm): 6.73 (d,  $J = 7.63$  Hz, 2 H, H-1',8'); 6.84 (d,  $J = 1.83$  Hz, 2 H, H-1,8); 7.15 (td,  $J = 7.63, 1.22$  Hz., 2 H, H-2',7'); 7.41 (td,  $J = 7.63, 1.22$  Hz, 2 H, H-3',6'); 7.48 (dd,  $J = 8.24, 1.83$  Hz, 2 H, H-3,6); 7.67 (d,  $J = 8.24$ ; 2 H; H-4,5); 7.85 (d,  $J = 7.63$ , 2 H, H-4',5').

m) Synthesis of 2,7-dicarbethoxy-9,9'-spirobifluorene

The Grignard reagent, prepared from 0.97 g (40 mmol) magnesium turnings and 9.32 g (6.8 ml, 40 mmol) 2-bromobiphenyl in 50 ml dry diethyl ether, is added dropwise over the course of 2 h to a boiling suspension of 13 g (40 mmol) 2,7-dicarbethoxy-9-fluorenone in 100 ml dry diethyl ether. After all the material has been added, it is boiled an additional 3 h. After cooling overnight, the precipitate is filtered off with suction and washed with cold ether. The magnesium complex that has been filtered off with suction is hydrolyzed in a solution of 15 g ammonium chloride in 250 ml ice water. After 1 h the 9-(2-biphenyl)-2,7-dicarbethoxy-9-fluorenol that has formed is filtered off with suction, washed with water, and suctioned dry. For the ring-closure reaction, the dried fluorenol is boiled in 100 ml glacial acetic acid for 6 hours after 3 drops concentrated HCL have been added. The result is allowed to crystallize overnight, the product that has formed is filtered off with suction, and it is washed with glacial acetic acid and water.

Yield: 15.1 g (82%) 2,7-dicarbethoxy-9,9'-spirobifluorene. For further purification, it can be recrystallized from ethanol.

$^1\text{H-NMR}$  ( $\text{CDCl}_3$ , ppm): 1.30 (t,  $J = 7.12$  Hz, 6 H, ester- $\text{CH}_3$ ); 4.27 (q,  $J = 7.12$  Hz, 4 H, ester- $\text{CH}_2$ ); 6.68 (d,  $J = 7.63$  Hz, 2 H, H-1',8'); 7.11 (td,  $J = 7.48, 1.22$  Hz, 2H, H-2',7'); 7.40 (td,  $J = 7.48, 1.22$  Hz, 4 H, H-1, 8, 3',6'); 7.89 (dt,  $J = 7.63, 0.92$  Hz, 2 H, H-4',5'); 7.94 (dd,  $J = 7.93, 0.6$  Hz, 2 H, H-4, 5); 8.12 (dd,  $J = 7.93, 1.53$  Hz, 2 H, H-3, 6).

n) Synthesis of 2,7-dibromo,2',7'-diiodo-9,9'-spirobifluorene

In a 250-ml three-necked flask with reflux condenser and dropping funnel, 5 ml water is added to a suspension of 2.37 g 2,7-dibromo-9,9'-spirobifluorene in 50 ml glacial acetic acid at  $80^\circ\text{C}$  and after the addition of 2 ml concentrated sulfuric acid, 1.27 g iodine, 0.53 g iodic acid and 5 ml carbon tetrachloride it was stirred until the iodine color disappeared.

The material is then filtered off with suction and washed well with water. After drying, the precipitate is dissolved in 150 ml dichloromethane and then washed successively with  $\text{Na}_2\text{SO}_3$  solution,  $\text{NaHCO}_3$  solution, and water. The dichloromethane phase is dried over  $\text{Na}_2\text{SO}_4$  and

then concentrated by evaporation. This produces colorless crystals of 2,7-dibromo,2',7'-diiodo-9,9'-spirobifluorene in quantitative yield. For additional purification, it can be recrystallized from dichloromethane/pentane.

$^1\text{H-NMR}$  ( $\text{CHCl}_3$ , ppm):

6.80 (d,  $J = 1.83$  Hz, 2 H), 6.99 (d,  $J = 1.53$  Hz, 2 H), 7.51 (dd,  $J = 8.24, 1.83$  Hz, 2 H), 7.54 (d,  $J = 7.93$  Hz, 2 H), 7.65 (d,  $J = 8.24$  Hz, 2 H), 7.72 (dd,  $J = 8.24, 1.53$  Hz, 2 H).

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## B. Examples of synthesis

### Example 1

2,2'-bis(benzofuran-2-yl)-9,9'-spirobifluorene  
(similar to W. Sahm, E. Schinzel, P. Jürges, Liebigs Ann. Chem. (1974) 523.)

2.7 g (22 mmol) salicylaldehyde and 5.0 g (10 mmol) 2,2'-bis(bromomethyl)-9,9'-spirobifluorene are dissolved at room temperature in 15 ml DMF and 0.9 g (22.5 mmol) pulverized NaOH and a spatula tip of KI are added. The mixture is heated to boiling and stirred for 1 h at the boiling temperature. After cooling, a mixture of 0.5 ml concentrated hydrochloric acid, 7 ml water, and 7 ml methanol are added to the reaction solution. The result is stirred another 1 h at room temperature, the crystalline reaction products are filtered off with suction, washed first with cold methanol, then with water, and dried under a vacuum at 60°C. This yields 4.6 g (79%) 2,2'-bis(2-formylphenyloxymethyl)9,9'-spirobifluorene.

2.1 g (22.5 mmol) freshly distilled aniline is added to 5.85 g (10 mmol) 2,2'-bis(2-formylphenyloxymethyl)9,9'-spirobifluorene in 10 ml toluene. A spatula tip of p-toluene sulfonic acid is added and the result is heated in a water separator until boiling, until no more water separates (ca. 3 to 5 h). Upon cooling of the reaction charge, the corresponding bis-benzylidenephénylamine precipitates out in crystalline form. It is filtered off with suction, washed with methanol, and dried under a vacuum at 60°C. For additional purification, it can be recrystallized from DMF.

7.35 g (10 mmol) of the bis-benzylidenephénylamine and 0.62 g (11 mmol) KOH are introduced under nitrogen into 30 ml DMF. The result is then heated to 100°C with stirring for 4 h. After cooling, the precipitate is filtered off with suction at room temperature and washed with a little DMF and water. After drying at 60°C in a vacuum drying oven, the 2,2'-



bis(benzofuran-2-yl)-9,9'-spirobifluorene can be purified by recrystallization from methyl benzoate.

#### Example 2

2,2',7,7'-Tetra(benzofuran-2-yl)-9,9'-spirobifluorene can be prepared in a manner similar to Example 1 with the corresponding change in stoichiometry.

#### Example 3

2,2',7,7'-Tetraphenyl-9,9'-spirobifluorene

5 g (7.9 mmol) 2,2',7,7'-tetrabromo-9,9'-spirobifluorene, 3.86 g (31.6 mmol) phenyl boric acid, 331.5 mg (1.264 mmol) triphenylphosphine and 70.9 mg (0.316 mmol) palladium acetate are slurried in a mixture of 65 ml toluene and 40 ml aqueous sodium carbonate solution (2 M). With strong stirring, the mixture is boiled for 24 h under reflux. After cooling, the result is filtered off with suction at room temperature, washed with water, and dried under a vacuum at 50°C. This yields 2.58 g. the filtrate is extracted with 50 ml toluene and the dried organic phase is concentrated by evaporation until dry. An additional 1.67 g is obtained.

Total yield: 4.25 g (86%)

#### Example 4

2,2',7,7'-Tetrakis-(biphenyl)-9,9'-spirobifluorene

5 g (7.9 mmol) 2,2',7,7'- tetrabromospirobifluorene, 6.57 g (33.2 mmol) biphenylboric acid, 331.5 mg (1.264 mmol) triphenylphosphine and 70.9 mg (0.316 mmol) palladium acetate are slurried in a mixture of 65 ml toluene and 40 ml aqueous sodium carbonate solution (2 M). With strong stirring, the mixture is boiled for 24 h under reflux. After cooling, the result is filtered off with suction at room temperature, washed with water, and dried under a vacuum at 50°C.

Yield: 5.95 g (81%)

## Example 5

## Synthesis of 2,2',7,7'-tetrabiphenyl-9,9'-spirobifluorene

In a 250-ml two-necked flask with reflux condenser and KPG stirrer, 5.5 g tetrabromospirobifluorene, 7.2 g biphenylboronic acid, and 400 mg tetrakis(triphenylphosphine)palladium are slurried in a mixture of 100 ml toluene and 50 ml potassium carbonate solution. While stirring with a KPG stirrer and under a blanket of inert gas, the mixture is boiled for 8 h under reflux. After cooling, the product is filtered off with suction and the precipitate is washed with water and dried. The toluene-phase is separated from the filtrate and the aqueous phase extracted by shaking in chloroform. The combined organic phases are dried over sodium sulfate and evaporated on a rotary evaporator, thereby yielding a second fraction of the product. The two product fractions are combined (8g) and dissolved in chloroform. The chloroform solution is boiled with activated carbon and filtered over a small column of silica gel. After evaporation on a rotary evaporator and recrystallization from chloroform/pentane, colorless crystals are obtained that fluoresce blue under UV light. Melting point 408°C (DSC).

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, ppm): 7.14 (d, J = 1.53 Hz, 4 H); 7.75 (dd, J = 7.93, 1.53 Hz, 4 H); 8.01 (d, J = 7.93 Hz, 4 H); 7.34 (dd, J = 7.32, 1.37 Hz, 4 H); 7.42 (t, J = 7.32 Hz, 8 H); 7.58 (24 H).

## Example 6

## Synthesis of 2,2',4,4',7,7'-hexabiphenyl-9,9'-spirobifluorene

In a 250-ml two-necked flask with reflux condenser and KPG stirrer, 1.6 g hexabromospirobifluorene and 3 g biphenylboronic acid are slurried in a mixture of 50 ml toluene and 50 ml 1 M potassium carbonate solution. The mixture is boiled under nitrogen under reflux and 115 mg tetrakis(triphenylphosphine)palladium in 5 ml toluene is added. The mixture is boiled under reflux for 7 h. After the reaction ends, the cooled solution is filtered and the filtrate shaken 2 x with water (chloroform is added for better phase separation). The organic phase is dried over sodium sulfate, filtered over a small column of silica gel, and then evaporated in a rotary evaporator. For additional purification, it is recrystallized from dichloromethane/pentane. This yields 2 g (80%) colorless crystals that fluoresce blue under UV light.

<sup>13</sup>C-NMR [360 MHz.; ATP, broadband decoupled] (CDCl<sub>3</sub>, ppm): 65.94 (1C, spiro-C); 126.95 (6C, CH), 126.97 (6C, CH), 127.17 (6C, CH), 127.35 (6C, CH), 127.36 (6C, CH), 127.39 (6C, CH), 127.52 (6C, CH), 128.73 (6C, CH), 128.75 (6C, CH), 128.94 (6C, CH), 129.90 (4 C, CH),

137.77 (2 C), 137.86 (2 C), 139.43 (2 C), 139.69 (2 C), 139.89 (2 C), 140.09 (2 C), 140.17 (2 C), 140.22 (2 C), 140.30 (2 C), 140.63 (2 C), 140.64 (2 C), 140.68 (2 C), 140.72 (2 C), 140.74 (2 C), 150.45 (2 C), 150.92 (2C).

#### Example 7

Synthesis of 2,2'-bis[(5(p-t-butylphenyl)-1,3,4-oxadiazol-2-yl)-9,9'-spirobifluorene from 9,9'-spirobifluorene-2,2'-dicarboxylic acid chloride and 5(4-t-butylphenyl)tetrazole

##### a) Synthesis of 5(4-t-butylphenyl)tetrazole

In a 250-ml round-bottomed flask with reflux condenser, 4.9 g p-t-butylbenzonitrile, 3.82 g lithium chloride, and 5.85 g sodium azide and 8.2 g triethylammoniumbromide in 100 ml DMF are heated for 8 h at 120°C. After cooling to room temperature, 100 ml water is added and dilute hydrochloric acid is added in an ice bath until no more precipitate separates out. The precipitate is filtered off with suction, washed with water, and dried.

Recrystallization from ethanol/water yields 4.4 g colorless crystals.

##### b) 9,9'-spirobifluorene-2,2'-dicarboxylic acid chloride

In a 100 ml flask with reflux condenser and drying tube, 2 g (5 mmol) 9,9'-spirobifluorene-2,2'-dicarboxylic acid is boiled for 4 h under reflux with 20 ml (freshly distilled) thionyl chloride and 3 drops DMF. After cooling, the reflux condenser is replaced with a distillation bridge and excess thionyl chloride is distilled off under a vacuum, 40 ml petroleum ether (30° -60°C) is added and distilled off, and the crystalline acid chloride remains.

##### c) 2,2'-Bis[(5(p-t-butylphenyl)-1,3,4-oxadiazol-2-yl)-9,9'-spirobifluorene

2.0 g (11 mmol) 5(4-t-butylphenyl)tetrazole dissolved in 20 ml anhydrous pyridine is added to the acid chloride and heated under reflux for 2 h under an inert gas. After cooling, the mixture is

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3 added to 200 ml water and allowed to stand for 2 h. The precipitated oxadiazole derivative is filtered off with suction, washed with water, and dried under a vacuum. Then it is chromatographed over silica gel with chloroform/acetic ester (99:1) and recrystallized from chloroform/pentane. 2.4 g colorless crystals are obtained.

<sup>1</sup>H-NMR (CDCl<sub>3</sub>, ppm):

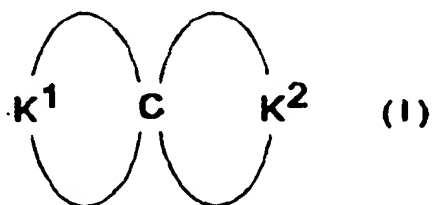
1.31 (s, 18 H, t-Butyl), 6.77 (d, J = 7.32 Hz, 2 H), 7.18 (td, J = 7.48, 1.22 Hz, 2 H), 7.44 (td, J = 7.40, 1.22 Hz, 2 H), 7.46 (d, J = 8.54 Hz, 4 H), 7.50 (d, J = 1.22 Hz, 2 H), 7.94 (d, J = 8.54 Hz, 4 H), 8.02 (d, J = 7.93 Hz, 6 H), 8.20 (dd, J = 7.93, 1.53 Hz, 2 H).

### C. Example application

2,2',7,7'-Tetrakis-(biphenyl)-9,9'-spirobifluorene is dissolved in chloroform (30 mg/ml) and applied by spin-coating (1,000 rpm) to a glass carrier coated with indium/tin oxide (ITO), whereby a homogeneous, transparent film is formed. An electrode of Mg/Ag (80/20) is applied to this film by vacuum deposition. When an electric voltage is applied between the ITO electrode and the metal electrode, where the metal electrode is negative with respect to the ITO electrode, a blue electroluminescence is observed.

### Claims

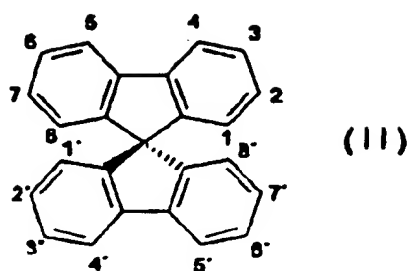
1. The use of spiro compounds of the general formula (I),



where

K<sup>1</sup> and K<sup>2</sup>, independently of each other, are conjugated systems in electroluminescence devices.

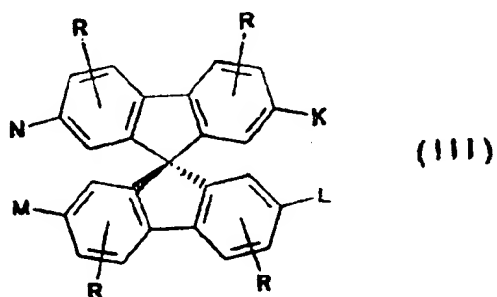
2. Use as recited in Claim 1, characterized in that a spirobifluorene of the general formula (II) is used,



where the benzo groups, independently of each other, can be substituted and/or fused.

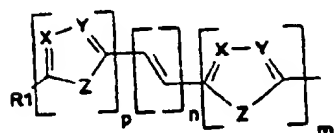
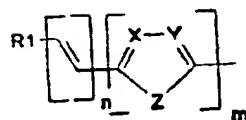
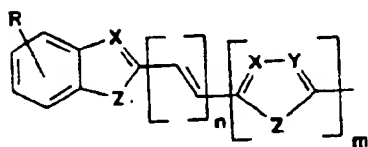
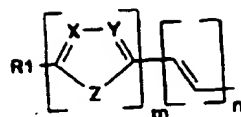
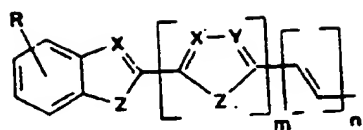
3. Use as recited in Claim 1 and/or 2, characterized in that a spirobifluorene derivative of the formula (III) is used,

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where the symbols and superscripts have the following meanings:

K, L, M, N are identical or different



R is identical or different and can have the same meanings as K, L, M, N or is -H, a linear or branched alkyl, alkoxy, or ester group with 1 to 22 C atoms, -CN, -NO<sub>2</sub>, -NR<sup>2</sup>R<sup>3</sup>, -Ar, or -O-Ar;

Ar is phenyl, biphenyl, 1-naphthyl, 2-naphthyl, 2-thienyl, 2-furanyl, where each of these groups may have one or two R residues,

m, n, p are 0, 1, 2, or 3;

X, Y are identical or different and are CR, N;

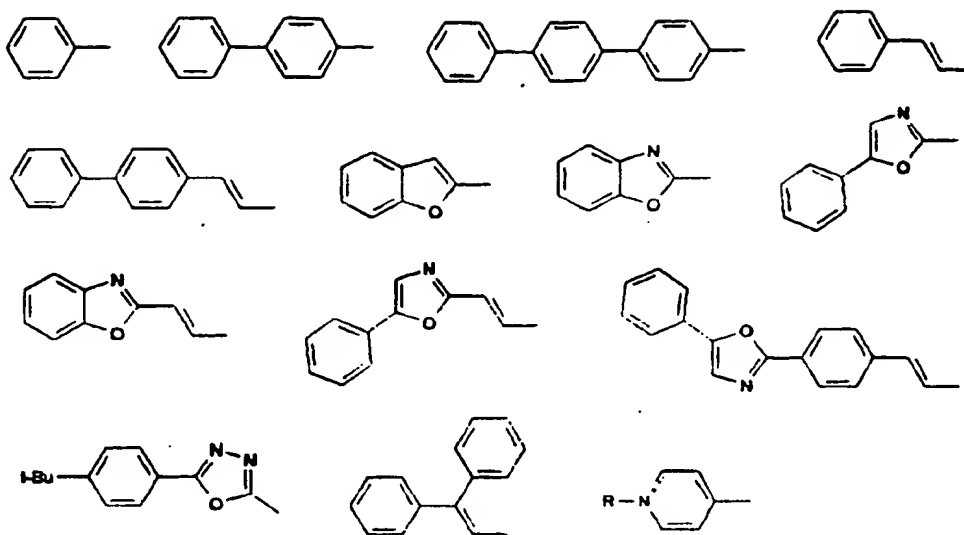
Z is -O-, -S-, -NR<sup>1</sup>-, -CR<sup>1</sup>R<sup>4</sup>-, -CH=CH-, -CH=N-;

R<sup>1</sup>, R<sup>4</sup> are identical or different and can have the same meaning as R;

R<sup>2</sup>, R<sup>3</sup> are identical or different and are H, a linear or branched alkyl group with 1 to 22 C atoms, -Ar, 3-methylphenyl.

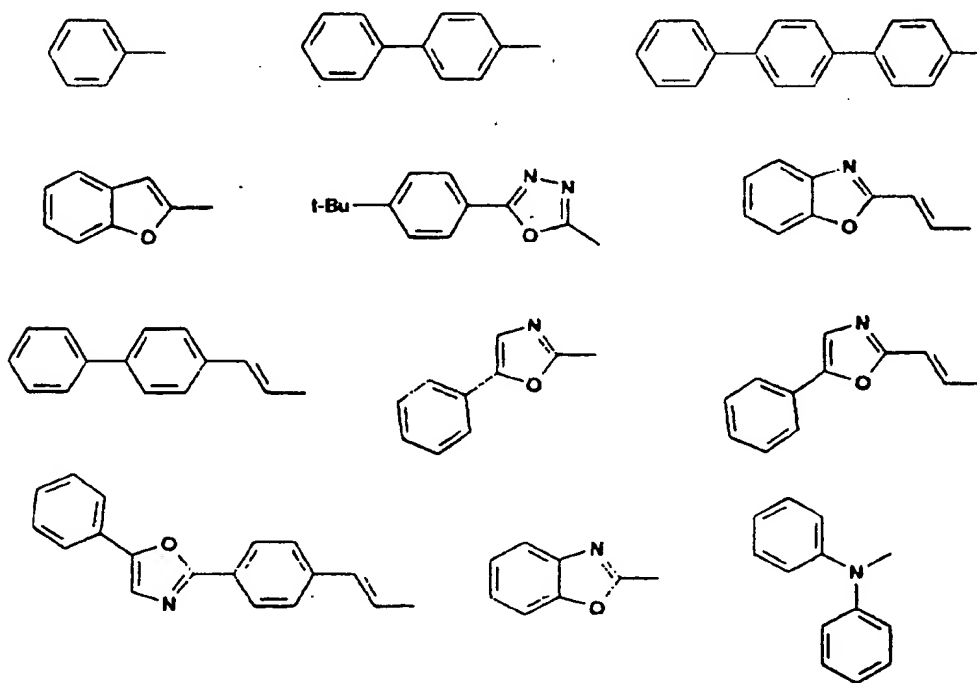
4. Use in accordance with one or more of the Claims 1 to 3, characterized in that a spirobifluorene derivative of the formula (IIIa) to (IIIg) is used,

IIIa) K = L = M = N and are from the group:

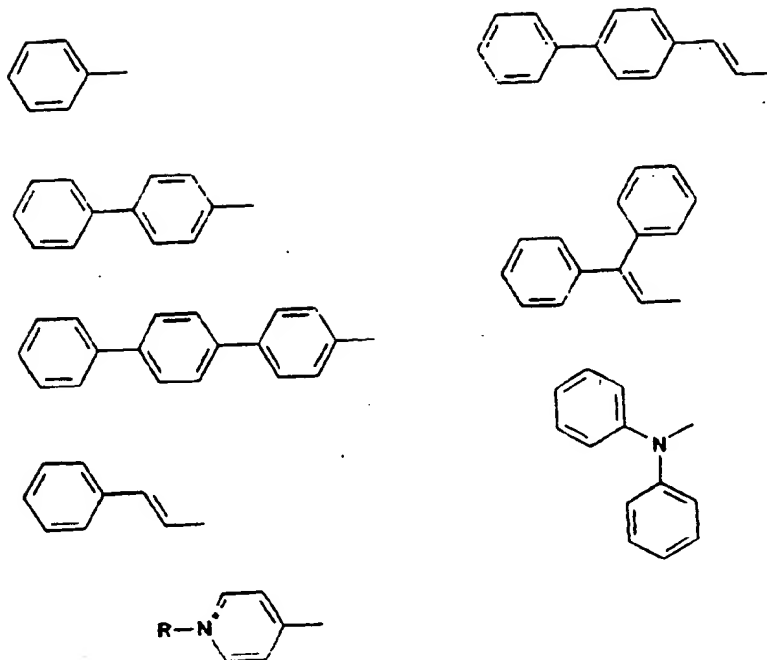


R = alkyl,  $C_2H_4SO_3-R = C_1-C_{22}$ -alkyl,  $C_2H_4SO_3-$

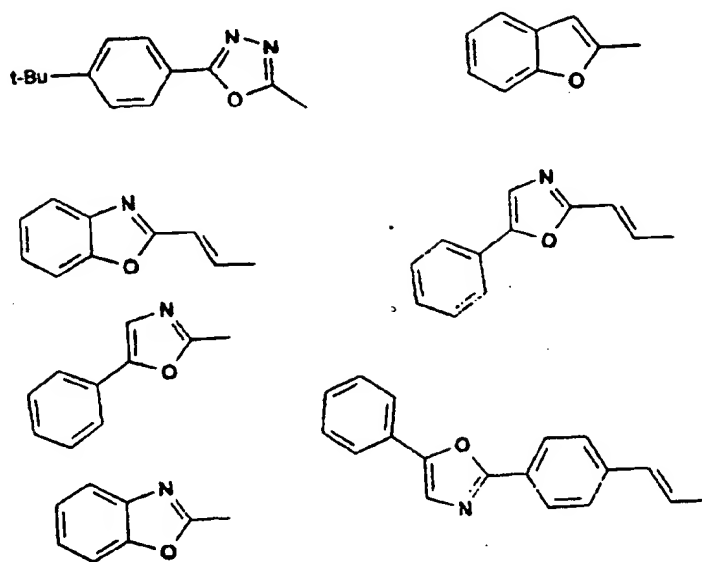
IIIIb) K = M = H and N = L and are from the group:



IIIIc) K = M and are from the group:

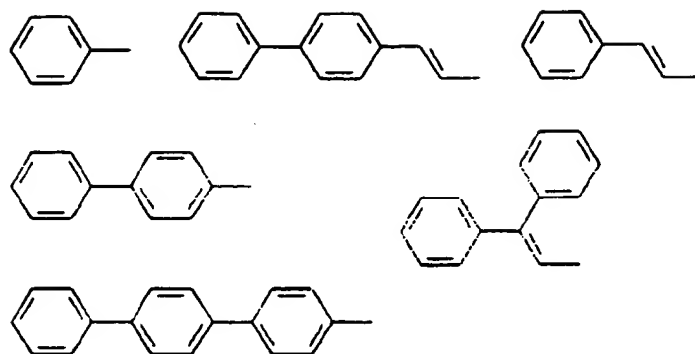


R = alkyl,  $C_2H_4SO_3^-$ , and N = L and they are from the group:

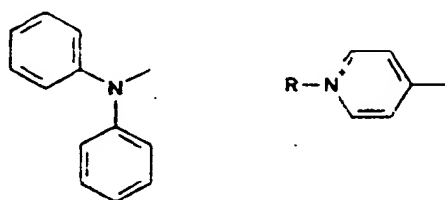


IIIId) K = M and they are from the group:



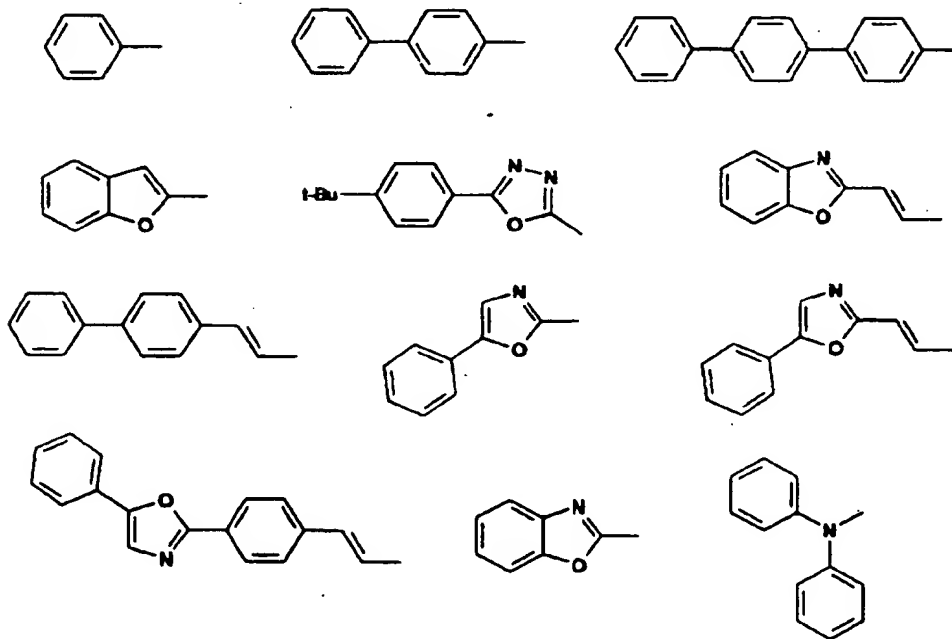


and  $N = L$  and they are from the group:

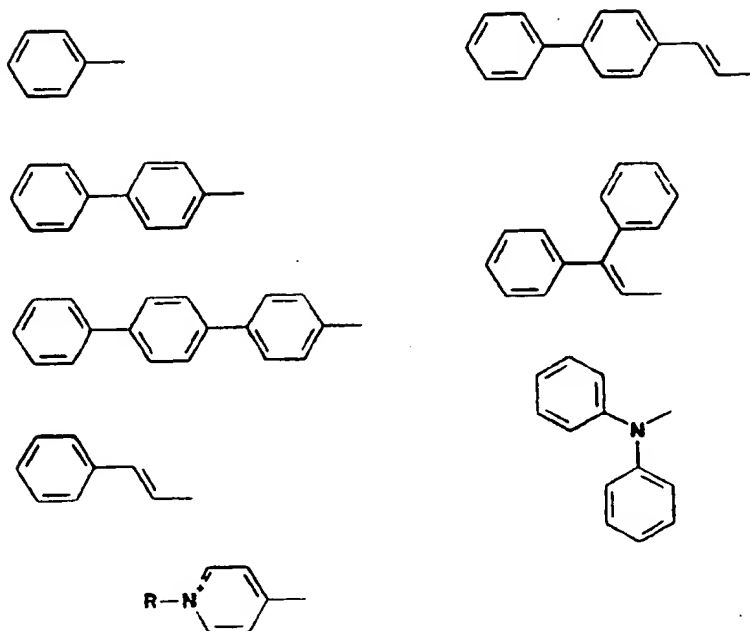


R = alkyl,  $C_2H_4SO_3^-$

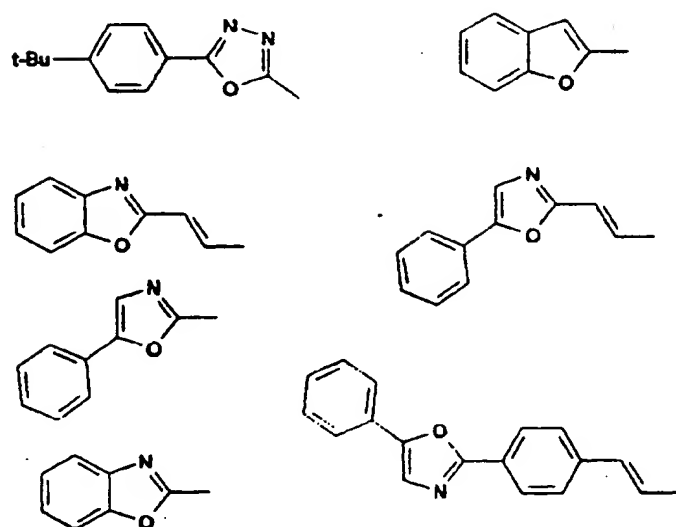
IIIe)  $K = L = H$  and  $M = N$  and they are from the group:



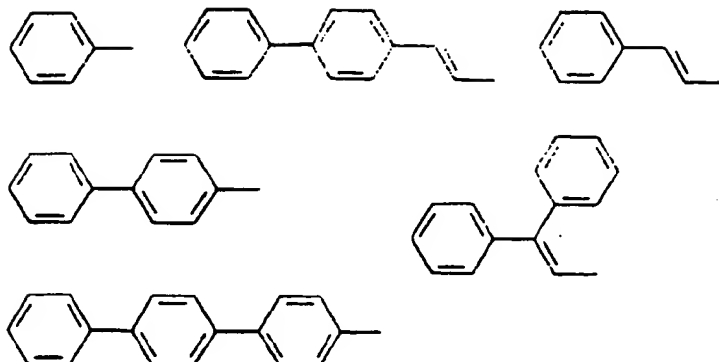
IIIIf)  $K = L$  and they are from the group:



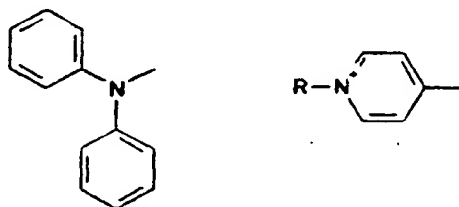
$R = \text{alkyl}, \text{C}_2\text{H}_4\text{SO}_3^-$  and  $M = N$  and they are from the group:



IIIIf)  $K = L$  and they are from the group:

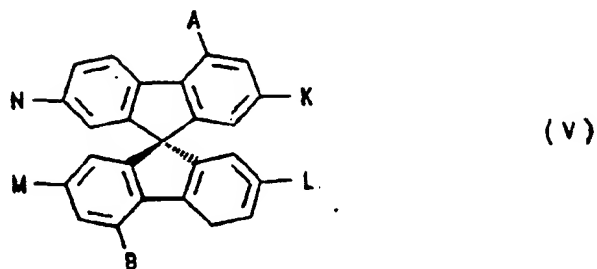


and  $M = N$  and they are from the group:



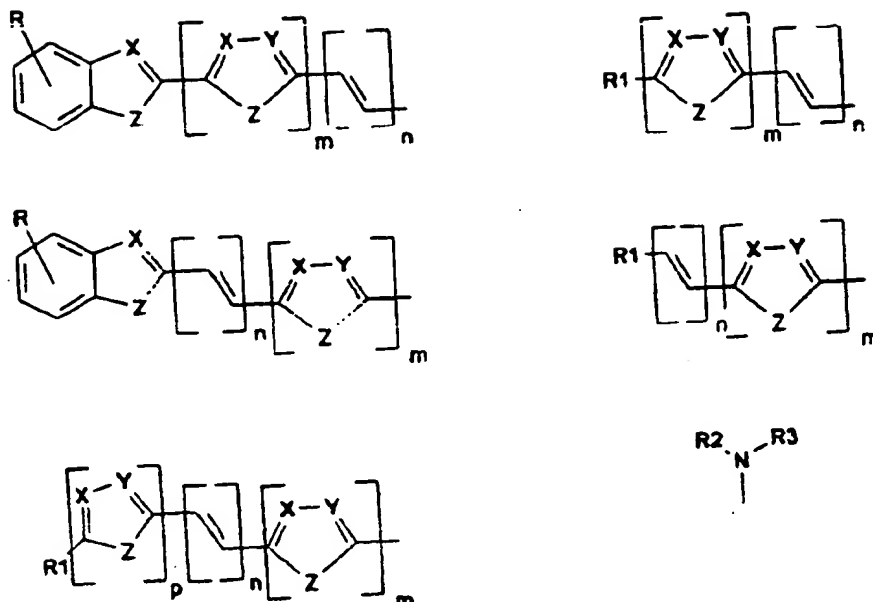
$R = \text{alkyl}, C_2H_4SO_3^-$

5. spiro compound of the formula (V),



where the symbols have the following meanings:

A, B, K, L, M, N are identical or different



and

A, B can also be identical or different and be a linear or branched alkyl, alkyloxy, or ester group with 1 to 22 C atoms, -CN, -NO<sub>2</sub>, -Ar or -O-Ar;

R is -H, a linear or branched alkyl, alkoxy, or ester group with 1 to 22 C atoms, -CN, -NO<sub>2</sub>, -NR<sup>2</sup>R<sup>3</sup>, -Ar, or -O-Ar;

Ar is phenyl, biphenyl, 1-naphthyl, 2-naphthyl, 2-thienyl, 2-furanyl, where each of these groups may have one or two R residues,

m, n, p are 0, 1, 2, or 3;

X, Y are identical or different and are CR, N;

Z is -O-, -S-, -NR<sup>1</sup>-, -CR<sup>1</sup>R<sup>4</sup>-, -CH=CH-, -CH=N-;

R<sup>1</sup>, R<sup>4</sup> are identical or different and can have the same meaning as R;

R<sup>2</sup>, R<sup>3</sup> are identical or different and are H, a linear or branched alkyl group with 1 to 22 C atoms, -Ar or 3-methylphenyl.

6. Use as recited in one or more of the Claims 1 to 5, characterized in that the spiro compound serves as a light-emitting layer.

7. Use as recited in one or more of the Claims 1 to 5, characterized in that the spiro compound serves as a transport layer.
8. Use as recited in one or more of the Claims 1 to 5, characterized in that the spiro compound serves for charge injection.
9. An electroluminescence device containing an active layer that contains one or more compounds of the formulas (I) to (III) as recited in one or more of the claims 1 to 4.
10. An electroluminescence device as recited in Claim 9, characterized in that the active layer is a light-emitting layer.
11. An electroluminescence device as recited in Claim 9, characterized in that the active layer is a transport layer.
12. An electroluminescence device as recited in Claim 9, characterized in that the active layer is a charge-injection layer.
13. An organic electroluminescent material, characterized in that its emission maximum in the region of 400 to 750 nm, measured at room temperature, is reduced by no more than 15%, relative to the initial state, after the material, applied at a thickness of no more than 1  $\mu\text{m}$  on a quartz substrate, is heated to 250°C for 30 min in an inert atmosphere at a pressure of no more than 1 mbar. /51
14. An organic electroluminescent material as recited in Claim 13, characterized in that the emission maximum is reduced by no more than 10%, relative to the initial state.
15. An organic electroluminescent material as recited in Claim 13 and/or 14, characterized in that the emission maximum is reduced by no more than 5%, relative to the initial state.
16. An organic electroluminescent material as recited in one or more of the Claims 13 to 15, characterized in that the emission maximum is not reduced, relative to the initial state.
17. An organic electroluminescent material as recited in one or more of the Claims 13 to 16, characterized in that the emission maximum increases, relative to the initial state.
18. An electroluminescence device containing an active layer that contains an electroluminescent material as recited in one or more of the Claims 13 to 17.

19. An electroluminescence device as recited in Claim 18,  
characterized in that the active layer is a light-emitting layer.

20. An electroluminescence device as recited in Claim 18,  
characterized in that the active layer is a transport layer.

21. An electroluminescence device as recited in Claim 18,  
characterized in that the active layer is a charge-injection layer.